JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC, PHYSIOLOGICAL, AND AGRICULTURAL CHEMISTRY.

1916. Vol. CX. Part I.

LONDON:

GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C.

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JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, **34**, 2455; *Bull. Soc. chim.* 1901, [iii], **25**, 794; *Gazzetta* 1901, **31**, i, 554.

ABBREVIATED TITLE.	JOURNAL.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Applicata.	Annali di Chimica Applicata.
Ann. Chim.	Annales de Chimie
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Ann. Soc. Quím. Argentina.	Annales de la Sociedad Química Argentina.
Arch. expt. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
* *Bied. Zentr.*	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Biochem. Bull.	Biochemical Bulletin.
Biochem. J.	The Biochemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bollettino chimico farmaceutico.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci. Roumaine.	Bulletin de la Section Scientique de l'Académie Roumaine.
Bull. Acad. Sci., Petrograd.	Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg.
Bull. Assoc. chim. Sucr. Dist.	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Zentr.*	Chemisches Zentralblatt.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.

* Abstracts from the *Zentralblatt* are made only in the case of papers published in journals other than those included in this list.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Int. Zeitsch. phys.-chem. Biol.	Internationale Zeitschrift für physikalisch-chemische Biologie.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik	Jahrbuch der Radioaktivität und Elektronik.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chim. phys.	Journal de Chimie physique.
J. Coll. Sci. Tokyo	Journal of the College of Science, Imperial Universit of Tokyo.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
K. Svenska Vet-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Kolloid Zeitsch.	Kolloid Zeitschrift.
Koll. Chem. Beihefte	Kolloidchemische Beihefte.
Lancet.	The Lancet.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Le Radium	Le Radium.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Kyōtō.	Memoirs of the College of Science, Kyōtō Imperial University.
Mem. Dept. Agric. India	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Metallurgie	Metallurgie.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Mon. Sci.	Moniteur Scientifique.
Nuovo Cim.	Il Nuovo Cimento.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Pharm. Zentr-h.	Pharmazeutische Zentralhalle.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc. London	Proceedings of the Physical Society of London.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. exp. Physiol.	Quarterly Journal of experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
Rev. de Métallurgie	Revue de Métallurgie.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Soil Sci.	Soil Science.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zeitsch. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Thermal Reactions of Petroleum Hydrocarbons in the Vapour Phase. WALTER F. RITTMAN (*J. Ind. Eng. Chem.*, 1915, **7**, 945—953. Compare A., 1914, i, 645, 793).—The study of the cracking of petroleum hydrocarbons of various types by heating in the vapour phase under varying conditions of temperature and pressure has been continued with the primary object of investigating the yields and the nature of the liquid products of the reaction. The cracking was conducted in an electrically heated furnace similar to that already described, and the pressures were self-generated by the cracked oil and regulated by a pressure release valve. The results of a large number of experiments are reproduced in tabular form, and comprise investigations of a Pennsylvania kerosene of which 90% boiled below 250°, an Oklahoma "fuel oil" of which only 22% distilled below 300°, a Californian asphaltic oil containing 17% boiling below 300°, and a Mexican oil of which 37% boiled below 300°. The products from these widely differing oils showed under similar conditions a remarkable similarity, the only noteworthy differences being in the amount of carbon deposit, whilst by suitable adjustment of conditions the type of the liquid product from any of the oils could be controlled. Gasolene production was favoured by temperatures of about 500° and pressures higher than 6 atm., and yields of 16—18% were observed. Low boiling aromatic hydrocarbons were produced in greatest amount at temperatures between 600° and 700° and pressures above 4 atm. The best yields lay

between 11 and 13%. Higher temperatures favour the production of carbon and gas at the expense of the liquid products. The course of the cracking process is one of dehydrogenation. The author considers that the aromatic hydrocarbons may be formed either by the dehydrogenation of naphthalene hydrocarbons, or by the splitting of polycyclic (asphaltic) hydrocarbons, or by the polymerisation of acetylenic hydrocarbons which are produced as intermediate products by the cracking of the higher paraffins or olefins.

G. F. M.

The Oxidising Effect of Sunlight. EYVIND BŒDTKER (*Bull. Soc. chim.*, 1915, [iv], **17**, 369—374).—$\beta\epsilon$-Dimethylhexane when exposed to sunlight in a loosely stoppered bottle for a long time yields a very small amount of a crystalline *compound*, $C_9H_{22}O_5$, m. p. 106°, which when dried in a vacuum over sulphuric acid loses water and is converted into a viscid liquid which soon blackens. The compound dissolves in water and alcohol. Its aqueous solution does not reduce ammoniacal silver nitrate or Fehling's solution, but it colours Schiff's reagent red.

*iso*Amyl nitrite when exposed to sunlight is easily decomposed, giving *methanetetracarboxylic acid*, $C(CO_2H)_4,5H_2O$, m. p. 132°, which gives a white, crystalline *barium* salt. When warmed on a water-bath the acid first loses its water of crystallisation, and then oxalic acid slowly sublimes. When heated at 180° the products of decomposition are oxalic acid and tartralic acid, $C_4H_4O_5$.

W. G.

***n*-Nonane.** LATHAM CLARKE and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1915, **37**, 2536—2538).—The authors have prepared *n*-nonane commencing with heptaldehyde. This substance, taken in the form of a fraction, b. p. 152—154°, obtained from the distillation of castor-oil, was converted by magnesium ethyl bromide into *n*-nonan-γ-ol (ethyl-*n*-hexylcarbinol; Gérard, A., 1907, i, 376), from which by the usual methods γ-iodononane and n-Δ^{β}-*nonylene*, a colourless, mobile liquid of pleasant, petroleum-like odour, b. p. 149·4—149·9°, D^{15} 0·7540, were successively produced. The last substance was reduced by passing its vapour mixed with hydrogen over freshly reduced nickel at 160°, the produced being *n*-nonane, a very mobile liquid of a very slight "sweetish" odour, b. p. 150·4—150·6°/759 mm., D^{15}_{15} 0·7219, n^{20}_{D} 1·4025.

D. F. T.

New Methods of Preparation of Erythrene. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1472—1494. Compare A., 1914, i, 474).—Erythrene may be obtained by the following twenty-nine new reactions, some of which may be used also for the preparation of homologues of erythrene, such as isoprene, piperylene, etc.:

I. Depolymerisation of cyclic hydrocarbons of terpenic character, (1) $CH\begin{matrix}\diagup CH_2\cdot CH_2 \diagdown \\ \diagdown CH-CH_2 \diagup\end{matrix}CH\cdot CHC{:}H_2 = 2CH_2{:}CH\cdot CH{:}CH_2$; in a similar way, cyclic dimethyldibutylene (the dimeride of 2:3-dimethyl-

erythrene) reacts with formation of 2:3-dimethylerythrene. II. Depolymerisation of open-chain hydrocarbons, accompanied by scission of either two hydrogen atoms or a molecule of a saturated hydrocarbon, (2) C_8H_{16}(dibutylene) = $2H_2 + 2CH_2{:}CH{\cdot}CH{:}CH_2$, (3) $C_{10}H_{20}$(diamylene) = $2CH_4 + 2CH_2{:}CH{\cdot}CH{:}CH_2$. These reactions are analogous to the known pyrogenation of natural myrcene, the dimeride of isoprene,

(4) $CH_2{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH_2 = 2CH_2{:}CMe{\cdot}CH{:}CH_2$.

III. The removal of RH, where R is an alkyl group, from saturated open-chain hydrocarbons, independently of their composition and structure, (5) $CH_2Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Me = 2CH_4 + CH_2{:}CH{\cdot}CH{:}CH_2$, or, in general, $R{\cdot}C_4H_8R' = RH + R'H + C_4H_6$, R and R′ being alkyl groups. This reaction takes place on pyrogenation of naphtha, dry distillation of coal, etc. IV. The removal of RH from an open-chain hydrocarbon containing one ethylene linking in its molecule, for instance, (6) $CMe_2{:}CHMe = CH_4 + CH_2{:}CH{\cdot}CH{:}CH_2$; this reaction may be regarded as an intermediate stage of reaction III. V. Removal of RH and hydrogen chloride from saturated, open-chain monochloro-derivatives of the aliphatic series, for instance, (7) $CMe_2Cl{\cdot}CH_2Me = CH_4 + HCl + C_4H_6$ and (8) $CHMe_2{\cdot}CH_2{\cdot}CH_2Cl = HCl + CH_4 + C_4H_6$. VI. Action of high temperatures on aromatic hydrocarbons, (9) $7C_6H_6 = 3C_6H_5Ph + C_2H_4 + H_2 + CH_2{:}CH{\cdot}CH{:}CH_2$. VII. Action of high temperatures on piperidine, (10) $2C_5H_{11}N = 2H_2 + 2CH_2{:}CH{\cdot}CH{:}CH_2 + N_2 + C_2H_6$ and $C_2H_6 = C_2H_4 + H_2$; the products include also hydrogen cyanide, pyridine, and resin. VIII. Removal of water from saturated four-membered cyclic alcohols,

$$(11)\ CH_2{<}{}^{CH_2}_{CH_2}{>}CH{\cdot}OH = H_2O + CH_2{:}CH{\cdot}CH{:}CH_2.$$

IX. Removal of hydrogen haloid from monohalogenated derivatives of saturated four-membered cyclic hydrocarbons,

$$(12)\ CH_2{<}{}^{CH_2}_{CH_2}{>}CHBr = HBr + CH_2{:}CH{\cdot}CH{:}CH_2.$$

X. Catalytic removal of 2 mols. of water from $\alpha\gamma$-glycols, (13) $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH = 2H_2O + CH_2{:}CH{\cdot}CH{:}CH_2$, and (14) $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH = 2H_2O + CH_2{:}CMe{\cdot}CH{:}CH_2$. XI. Catalytic removal of water and acid from esters of $\alpha\gamma$-glycols,

$$(15)\ OAc{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OH = H_2O + C_2H_4O_2 + C_4H_6,$$
$$(16)\ OAc{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OAc = 2C_2H_4O_2 + C_4H_6,$$
$$(17)\ OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}CHMe{\cdot}OH = 2H_2O + CHMe{:}CH{\cdot}CO_2H + C_4H_6.$$

XII. Catalytic removal of a molecule of acid from esters of Δ^{β}-buten-ol, (18) $CHMe{:}CH{\cdot}CH_2{\cdot}OAc = C_2H_4O_2 + C_4H_6$, Δ^{β}-butenyl acetate being obtained by the action of magnesium amalgam on aldol, $3OH{\cdot}CHMe{\cdot}CH_2{\cdot}CHO = 2H_2O + CHMe{:}CH{\cdot}CH_2{\cdot}OAc$. XIII. Catalytic removal of $2H_2O$ from hydroxy-ethers, (19) $OH{\cdot}CHMe{\cdot}OEt = 2H_2O + C_4H_6$. XIV. Catalytic scission of 1 mol. of hydrogen haloid and 1 mol. of water from chloro-ethers, (20) $CHMeCl{\cdot}OEt = H_2O + HCl + C_4H_6$; the compound, $CH_2Cl{\cdot}CH_2{\cdot}OEt$, also gives erythrene under the same conditions. XV. Catalytic scission of 1 mol. of alcohol and 1 mol.

of water from acetals, (21) $OEt\cdot CHMe\cdot OEt = H_2O + Et\cdot OH + C_4H_6$ and $Et\cdot OH = H_2O + C_2H_4$. XVI. Catalytic scission of 1 mol. of water and 1 mol. of acid from esters of hydroxyethyl ethyl ether, (22) $OAc\cdot CHMe\cdot OEt = H_2O + AcOH + C_4H_6$. XVII. Catalytic removal of water from vinyl ethyl ether, (23) $CH_2{:}CH\cdot OEt = H_2O + C_4H_6$. XVIII. Catalytic removal of water from tetrahydrofuran, (24) $O{<}{\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{smallmatrix}} = H_2O + C_4H_6$. XIX. Condensation of different alcohols with various aldehydes, accompanied by liberation of 2 mols. of water, (25) $CH_3\cdot CHO + Et\cdot OH = 2H_2O + C_4H_6$,

(26) $CH_3\cdot CHO + CHMe_2\cdot OH = 2H_2O + CHMe{:}CH\cdot CH{:}CH_2$.

XX. Condensation of ethyl alcohol with dihalogenated ethanes,

(27) $CH_2Br\cdot CH_2Br + Et\cdot OH = 2HBr + H_2O + C_4H_6$,

(28) $CH_2MeBr_2 + Et\cdot OH = 2HBr + H_2O + C_4H_6$.

XXI. Condensation of ethyl alcohol with vinyl bromide,

(29) $CH_2{:}CHBr + Et\cdot OH = H_2O + HBr + C_4H_6$.

A detailed discussion is given of the practical applicability of the different processes for converting ethyl alcohol into erythrene, acetic acid, etc., and of the uses to which the by-products may be put.

T. H. P.

Condensation of Alcohols and Aldehydes in Presence of Dehydrating Agents: Mechanism of the Process. I. I. Ostromisslenski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1494—1506).—It has been already shown that, in the presence of catalytic dehydrating agents, such as red phosphorus, glacial phosphoric acid, sulphanilic acid, barium chloride, and particularly alumina in the form of "argilla pura," acetaldehyde or paracetaldehyde condenses with alcohol, yielding erythrene, $CH_3\cdot CHO + Et\cdot OH = 2H_2O + CH_2{:}CH\cdot CH{:}CH_2$. It is now shown that in this reaction the following intermediate compounds are formed: α-hydroxyethyl ethyl ether, $\alpha\gamma$-dihydroxybutane, δ-hydroxy-Δ^{β}-butylene, and methylallene, the various stages being represented by the following equations: $CH_3\cdot CHO + Et\cdot OH \rightleftarrows OH\cdot CHMe\cdot OEt$, $CH_3\cdot CHO + Et\cdot OH + OH\cdot CHMe\cdot OEt = 2OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH$,

$OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot OH = H_2O + CHMe{:}CH\cdot CH_2\cdot OH$,

$CHMe{:}CH\cdot CH_2\cdot OH = H_2O + CHMe{:}C{:}CH_2$ and $CHMe{:}C{:}CH_2 = CH_2{:}CH\cdot CH{:}CH_2$.

T. H. P.

New Method of Preparing Piperylene. I. I. Ostromisslenski and P. N. Rabinovitsch (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1507—1509).—In presence of alumina at about 400°, propyl or *iso*propyl alcohol condenses with acetaldehyde, with formation of piperylene, thus:

$$CHMe_2\cdot OH + CH_3\cdot CHO = OH\cdot CHMe\cdot CH_2\cdot CHMe\cdot OH = 2H_2O + CHMe{:}CH\cdot CH{:}CH_2;$$

no trace of isoprene is formed. This method is recommended as the cheapest and simplest means of preparing piperylene.

T. H. P.

Condensation of Mixtures of Acetaldehyde and Alcohol to Erythrene. I. I. OSTROMISSLENSKI and S. S. KELBASINSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1509—1528).—A considerable number of experiments have been made to determine the effects of the different factors influencing the yield of erythrene obtained when the vapours of acetaldehyde and alcohol are heated together in presence of alumina. The results are given in detail, and are mostly of technical interest only.

Precipitated alumina gives the best results, but its action is due partly to the various impurities, such as basic ammonium and aluminium salts, sulphates, etc., present. The form and degree of fineness of the alumina are of little influence, but as the reaction proceeds throughout the whole mass, and not merely at the surface of the alumina, the latter must be sufficiently porous and hygroscopic. "Fatigue" of the catalyst is conditioned by the formation of resinous and carbonaceous products of the reaction, and may be remedied by heating to redness and subsequent treatment with water at the ordinary temperature of the snow-white alumina thus obtained; regenerated alumina gives results identical with those furnished originally. The best temperature for the alumina is 360—460°, the mixed vapours being heated rapidly to this temperature and the products of the reaction quickly removed from the region of high temperature. The nature of the material of the tube containing the alumina exerts marked influence on the yield of erythrene, this being to some extent determined by its thermal conductivity. Mixtures containing 1, 1·5, or 2 parts of alcohol to 1 part of acetaldehyde give approximately identical yields of erythrene, 100 parts by weight of such mixture giving up to 25 parts of crude product and 16—18 parts of pure erythrene. This result may be due partly to lowering of the partial pressures of the reacting substances by the excess of alcohol; it is, however, possible that some proportion of the excess of alcohol is converted into acetaldehyde and hydrogen, since the latter is actually found among the products; the preliminary formation of acetal according to the equation $2Et{\cdot}OH + CH_3{\cdot}CHO = OEt{\cdot}CHMe{\cdot}OEt$ is also possible, it having been shown previously that this acetal gives good yields of erythrene under the conditions employed. As the reaction, $Et{\cdot}OH + CH_3{\cdot}CHO = 2H_2O + CH_2{:}CH{\cdot}CH{:}CH_2$, is accompanied by increase in the volume of vapour, it should be favoured by diminished pressure; this is actually found to be the case.

T. H. P.

Isoprene from β-Pinene. A. W. SCHORGER and R. SAYRE (*J. Ind. Eng. Chem.*, 1915, **7**, 924—926).—When treated under similar conditions in a modification of Harries' isoprene lamp (A., 1911, i, 798) provided with a reflux arrangement to return the fractions of higher boiling point to the flask, α- and β-pinene gave each about a 10% yield of isoprene. Since nichrome heating wires gave an entirely different result from platinum wires, becoming coated with a thick deposit of carbon, the conclusion is drawn that the action of the platinum is a catalytic one. Similar yields

of isoprene were obtained from α- and β-pinene by passing the vapours slowly through an iron tube filled with pumice impregnated with platinum black, and heated to a barely visible red heat. The authors regard dipentene as an intermediate product in the formation of isoprene by these reactions, but oppose Harries' view (*loc. cit.*) that it originates from dipentene initially present in the pinene. G. F. M.

Vapour Pressures of Acetylene, Ammonia and *iso*Butane at Temperatures below their Normal Boiling Points. G. A. BURRELL and I. W. ROBERTSON (*J. Amer. Chem. Soc.*, 1915, **37**, 2482—2486).—Using the method previously adopted (A., 1915, i, 861, 933), the authors have determined the vapour pressures of acetylene, ammonia, and *iso*butane at low temperatures, and have obtained the following results. For acetylene the vapour pressure ranges from 760 mm. at $-83{\cdot}9^\circ$ to $1{\cdot}0$ mm. at $-143{\cdot}1^\circ$; for *iso*butane from 760 mm. at $-13{\cdot}3^\circ$ to $1{\cdot}0$ mm. at $-114{\cdot}7^\circ$, and for ammonia 760 mm. at $-34{\cdot}5^\circ$ to 1 mm. at $-13{\cdot}2^\circ$. The experimental results agree well, on the whole, with the corresponding values calculated from the Nernst equation. The equations representing the vapour-pressure curves are deduced, and found to be, for acetylene,

$$\log P = -957{\cdot}21/T + 1{\cdot}75 \log T - 0{\cdot}001511T + 3{\cdot}6728;$$

for *iso*butane,

$$\log P = -1632{\cdot}661/T + 1{\cdot}75 \log T - 0{\cdot}0158873T + 9{\cdot}06814;$$

for ammonia,

$$\log P = -1951{\cdot}72/T + 1{\cdot}75 \log T - 0{\cdot}015525T + 10{\cdot}6063.$$

The heats of vaporisation are calculated from the Clausius-Clapeyron equation, and found to be, for ammonia 6271 cal., for acetylene 5152 cal., and for *iso*butane 4828 cal. The vapour-pressure values of ammonia are compared with similar values found by Brill (A., 1906, ii, 847), and shown to agree fairly well. J. F. S.

An Improved Method for the Preparation of Allyl Alcohol, together with a Critical Examination of the Methods Hitherto Used. AGNES HOFF (*K. Danske Videnskab. Selskab. Forhand.*, 1915, Nos. 3—4, 199—224).—The author has investigated the following methods for the preparation of allyl alcohol: (1) reduction of acraldehyde; (2) action of sodium on dichlorohydrin; (3) hydrolysis of allyl iodide; (4) reduction of glycerol with oxalic acid. From a preparative point of view, no one is found to be as satisfactory as the following method, depending on the direct reduction of glycerol with formic acid. 825 Grams of 97% glycerol and $84{\cdot}2$ grams of 95% formic acid, that is, glycerol and formic acid in the molecular proportion of 5 : 1, are heated together in a retort; the receiver is changed at 200°, and the distillate collected between 200° and 250°. After cooling, a further quantity of 165 grams of glycerol and $84{\cdot}2$ grams of formic acid are added, and the distillation carried out as before. This process is repeated ten times. From the distillate between 200° and 250°, which

weighs about 1470 grams, allyl alcohol is obtained in the usual way by appropriate treatment with potassium carbonate, the yield being about 54%, calculated either with respect to the glycerol or the formic acid [compare Chattaway, T., 1915, **107**, 407].

T. S. P.

The Action of Aluminium Chloride on the Aliphatic Ethers. G. B. FRANKFORTER and E. A. DANIELS (*J. Amer. Chem. Soc.*, 1915, **37**, 2560—2567).—Having already discovered that phenyl methyl ether reacts with chloral in the presence of aluminium chloride at low temperatures according to the equation

$$2C_6H_5{\cdot}OMe + CHO{\cdot}CCl_3 = (OMe{\cdot}C_6H_4)_2CH{\cdot}CCl_3 + H_2O,$$

the authors have examined the behaviour of ethyl ether under similar treatment, but have obtained no definite product, the reaction apparently being very complex. The investigation, however, led them to an examination of the additive compound $AlCl_3,Et_2O$ obtainable from absolute ether and aluminium chloride (compare Walker and Spencer, T., 1914, **85**, 1106); this substance forms platelets, m. p. 33—35°, which are decomposed by water or heating at 106°, with formation of a basic chloride approximating to the composition $3Al(OH)_3,2Al(OH)_2Cl$. *n*-Propyl ether also gave an additive compound, approximating to the composition $AlCl_3,Pr_2O$, which was a red liquid less reactive than the ethyl ether analogue.

Aluminium chloride dissolves in anhydrous ether to a clear solution, but if water is present a cloudiness or precipitate is produced. This behaviour can therefore be used as a test for the presence of water in ether; the test will detect the presence of one drop of water in 500 c.c. of anhydrous ether, but is vitiated by the simultaneous presence of more than 5% of alcohol.

D. F. T.

The Change of Ammonium Isethionate by Heating. K. MIYAKE (*J. Amer. Chem. Soc.*, 1915, **37**. 2604).—The statements of Strecker (*Annalen*, 1854, **91**, 97) and Carl (A., 1881, 581) as to the effect of heat on ammonium isethionate are conflicting, and the author after several fruitless attempts to prepare taurine in the manner described by Strecker has come to the conclusion that Carl's view of the change is the correct one. D. F. T.

Diagram of State of the System Formed by Sodium and Potassium Acetates. A. BASKOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1533—1535).—The melting-point diagram of this system shows that sodium acetate (m. p. 320°) and potassium acetate (m. p. 295°) form solid solutions in all proportions. The minimum melting point is about 233°, and corresponds with approximately 46 mol. % of sodium acetate. None of the cooling curves shows a eutectic point, but the initial and final temperatures of crystallisation are sharply defined; when one of the components predominates, the initial exceeds the final temperature by 8·5—19·5°, or, on the average, 12°. The exact determination of the electrical conductivities of the system by Kohlrausch's method with an

alternating current is difficult, owing to the deposition on the platinised platinum electrodes of small amounts of gas-bubbles derived from decomposition of the electrolyte. At 325° the specific conductivity of fused potassium acetate is about 4·2 mhos, which is lowered to 3·9, 2·7, and 2·1 mhos by 10%, 20%, and 38% respectively of the sodium salt; for the latter in the pure state the value is 5·2 mhos. The conductivities of the fused mixtures increase continuously when the temperature is raised from 295° to 350°. T. H. P.

Some Salts of the Halogenoacetic Acids. II. W. G. BATEMAN and D. B. CONRAD (*J. Amer. Chem. Soc.*, 1915, **37**, 2553—2550).—A continuation of the earlier publication (Bateman and Hoel, A., 1915, i, 4).

The following salts are described: *ammonium dichloroacetate*, pearly leaflets; ammonium bromoacetate, leaflets; copper dichloroacetate, pale, bluish-green needles, or, with $4H_2O$, deep blue needles; copper trichloroacetate, a bright, bluish-green powder, or, with $3H_2O$, blue crystals; copper bromoacetate, bluish-green, or, with $1H_2O$, green crystals; mercuric chloroacetate, leaflets, m. p. 135°, b. p. 140° (decomp.); mercuric trichloroacetate, needles; mercurous trichloroacetate, needles, very soluble in the ordinary organic solvents; mercurous dichloroacetate, needles; mercurous bromoacetate, amorphous, white powder.

The above copper salts are reduced by phenylhydrazine, the reactions being complex. Ammonium dichloroacetate reacts with hydrogen chloride in ethyl acetate solution, giving a precipitate of ammonium chloride. D. F. T.

Preparation of Organic Anhydrides, and of Corresponding New Industrial Products and their Technical Applications. G. BOITEAU (*Fr. Pat.* 474828; from *J. Soc. Chem. Ind.*, 1915, **34**, 1116). —Carboxylic acids on treatment with acetylene in presence of a catalyst, such as a mercury salt, are converted into the corresponding anhydrides. A small quantity of an oxidising agent, as, for example, potassium dichromate, is added at the beginning of the reaction. Acetic acid when treated in this way is converted into a mixture of acetic anhydride and ethylidene diacetate, which may either be used as a solvent for cellulose acetate or other cellulose compounds, or it may be separated into acetic anhydride and acetaldehyde by fractional distillation. G. F. M.

Preparation of Optically Active Fats. III. Synthesis of the Four Possible Optically Active Butyrins. Rearrangement of the 3-Carbon System into the Optical Antipodes. EMIL ABDERHALDEN and EGON EICHWALD (*Ber.*, 1915, **48**, 1847—1865. Compare A., 1914, i, 801; 1915, i, 115, 210).—The authors have not yet been able to devise a rapid method for converting the active dibromohydrins into active aminoglycerol and active fats. In the course of the investigation they have made the discovery that although *d*-monobromohydrin reacts with ammonia, giving

d-aminoglycerol, similar treatment of *d*-dibromohydrin yields an inactive diamino-compound. This result appears to confirm the view that the action is not a mere substitution of NH_2 for a halogen atom, and that a glycide ring is intermediarily produced at which an additive action occurs, thus:

$$CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}OH \longrightarrow CH_2Br{\cdot}\underset{CH_2}{\overset{|}{CH}}\!\!>\!O \longrightarrow$$

$$CH_2Br{\cdot}CH(OH){\cdot}CH_2{\cdot}NH_2 \longrightarrow$$

$$O\!<\!\!\begin{array}{l}CH{\cdot}CH_2{\cdot}NH_2\\ CH_2\end{array} \longrightarrow NH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NH_2.$$

Other reactions also seem to involve some such mechanism, for example, epibromohydrin reacts with an alcoholic solution of potassium iodide, giving an inactive epi-iodohydrin, and inactive products are also obtained in the interaction of dibromohydrin and bromohydrin with silver salts or alkali salts of the fatty acids, although according to the usual representation of the chemical change the asymmetric atom would appear to be unaffected. The active amino-glycerols are free from this defect for synthetic purposes, and for the protection of the amino-group it is advisable to use the sulphate or a solution in sulphuric acid; in this way, by heating with an excess of the fatty acid, esterification can be effected, and the amino-group can be subsequently eliminated by treatment with sodium nitrite. It is important to note that whereas *l*-epihydrin alcohol in direct reaction with butyric acid yields a dextrorotatory monobutyrin, the same substance is convertible into *d*-aminoglycerol, which, by way of an aminobutyrin, yields a lævorotatory butyrin. A molecular rearrangement therefore probably occurs, and it should, as a consequence, be possible to effect a rearrangement from an optically active substance to its enantiomorph by converting the compound $NH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br$ into $OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}NH_2$ (by several stages) and passing from the latter to $CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}NH_2$.

A transformation of an even simpler kind has been achieved by starting with *d*-epibromohydrin; this can be converted by addition of hydrogen chloride into active chlorobromopropan-β-ol, $CH_2Br{\cdot}CH(OH){\cdot}CH_2Cl$, which on elimination of hydrogen bromide by means of aqueous potassium hydroxide gives *l*-epichlorohydrin. This substance can be made to yield the enantiomorphs of the compounds given by *d*-epibromohydrin, namely, *d*-formylchlorohydrin, *l*-chlorohydrin, and *d*-epihydrin alcohol, which last can be converted on the one hand into *l*-monobutyrin and on the other through *l*-aminoglycerol into *d*-dibutyrin. In this way, therefore, it is possible to pass from *d*-epibromohydrin to enantiomorphous monobutyrins and dibutyrins in addition to other products. As a consequence of the result that a compound of the type

$$\overset{\displaystyle O}{\overbrace{\underset{\gamma}{CH_2}{\cdot}\underset{\beta}{CH}}}{\cdot}\underset{\alpha}{CH_2}{\cdot}OH$$

gives a *d*- or *l*-derivative, according to whether

the fatty acid is introduced at position α or γ, there can be no rigid classification according to constitution, and the terms *d*- and *l*- are used by the authors merely with reference to optical activity.

d-α-Monobromohydrin ($[\alpha]_D^{18}$ +4·10° in water) was converted into the following derivatives: by treatment with propionic anhydride into d-α-*bromodipropionylhydrin*,

$CH_2Br\cdot CH(O\cdot COEt)\cdot CH_2\cdot O\cdot COEt$,

$[\alpha]_D^{18}$ −2·21° in alcohol; by treatment with butyryl chloride into d-α-*bromodibutyrylhydrin*, $[\alpha]_D^{18}$ −2·19° in alcohol; by treatment with alcoholic potassium hydroxide solution into *l*-epihydrin alcohol (described as *d*- in the earlier publication), $[\alpha]_D^{18}$ −8·55°, which could be converted into *d*-aminoglycerol, b. p. 134°/0·1 mm., $[\alpha]_D^{18}$ +2·42° in water, +17·70° in dilute hydrochloric acid.

l-Epihydrin alcohol, $[\alpha]_D^{18}$ −8·55°, was converted into the following monoglycerides: monoformin, inactive; *l*-α-monoacetin, $[\alpha]_D^{18}$ −1·14°; *l*-α-monopropionin, $[\alpha]_D^{18}$ −0·83°; *l*-α-monobutyrin, $[\alpha]_D^{18}$ −0·63°; *d*-α-monobutyrin, $[\alpha]_D^{18}$ +0·83°; *l*-α-monovalerin, $[\alpha]_D^{18}$ −0·53°; *l*-α-monohexoin, $[\alpha]_D^{18}$ −0·40°, the optical rotations being all determined in alcoholic solution.

By treating *d*-aminoglycerol hydrochloride with butyryl chloride and adding sodium nitrite to the cooled solution of the product, there was obtained *l*-dibutyrin, b. p. 134—136°/0·5 mm., which was obtained in a purer condition by heating aminoglycerol sulphate with butyric acid at 65°, and then keeping the mixture for two to three days at the ordinary temperature; the d-γ-*amino*-$\alpha\beta$-*dibutyrin*, $NH_2\cdot CH_2\cdot CH(O\cdot COPr)\cdot CH_2\cdot O\cdot COPr$, a basic oil, $[\alpha]_D^{18}$ +0·47° in alcohol, +1·09° in dilute hydrochloric acid, thus produced was convertible by nitrous acid into l-$\alpha\beta$-*dibutyrin*, $OH\cdot CH_2\cdot CH(O\cdot COPr)\cdot CH_2\cdot O\cdot COPr$, $[\alpha]_D^{18}$ −1·10° in liquid state, −0·98° dissolved in alcohol. In a similar manner to the last, l-$\alpha\beta$-*dihexoin*, $[\alpha]_D^{18}$ −0·25° in carbon tetrachloride, +0·57° in chloroform, and −0·44° in light petroleum, was prepared.

From *l*-dibutyrin it was possible to obtain three triglycerides, all of which were only feebly active: l-α-*lauro*-$\beta\gamma$-*dibutyrin*, obtained by the action of lauryl chloride, was an oily fat; l-α-*stearo*-$\beta\gamma$-*dibutyrin* and l-α-*oleo*-$\beta\gamma$-*dibutyrin* were prepared in a similar manner, the former being a solid substance, m. p. 15°.

When shaken with 15% hydrochloric acid solution, *d*-epibromohydrin is converted into d-α-*chloro*-γ-*bromopropan*-β-*ol*,

$CH_2Br\cdot CH(OH)\cdot CH_2Cl$,

b. p. 88°/15 mm., $[\alpha]_D^{18}$ +0·64°, which on treatment with potassium hydroxide solution eliminates hydrogen chloride, with formation of l-*epichlorohydrin*, b. p. 92—93°/360 mm., $[\alpha]_D^{18}$ −25·61°; this with formic acid yielded *d*-formyl-α-chlorohydrin, which on hydrolysis with hydrochloric acid gave *l*-monochlorohydrin, $[\alpha]_D^{18}$ −1·88° in water. d-*Epihydrin alcohol*, $[\alpha]_D^{18}$ +7·69°, obtained from the last substance, reacted with butyric acid, giving l-*monobutyrin*, $[\alpha]_D^{18}$ −0·84°, and was converted by way of *l*-aminoglycerol, $[\alpha]_D^{18}$ −14·08° in dilute hydrochloric acid, into *d*-dibutyrin, $[\alpha]_D^{18}$ +1·01° in liquid state.

D. F. T.

Synthesis of Normal Tridecoic and Tetracosanic Acids. P. A. LEVENE, C. J. WEST, C. H. ALLEN, and J. VAN DER SCHEER (*J. Biol. Chem.*, 1915, **23**, 71—75).—Tridecoic acid, $C_{12}H_{25}\cdot CO_2H$, has been previously obtained by Levene and West by the oxidation of α-hydroxymyristic acid, and was found to have a higher m. p. than was expected (A., 1914, i, 1122). It has now been prepared by the action of undecyl iodide on sodium ethyl malonate, followed by saponification of the ester obtained to undecylmalonic acid; the latter on heating yelds tridecoic acid, having the same m. p. (44·5—45·5°) as that prepared by the other method. The properties of the substances prepared in the course of the synthesis are as follows: undecyl alcohol, $C_{11}H_{23}\cdot OH$, b. p. 147°/25 mm.; undecyl iodide, $C_{11}H_{23}I$, b. p. 125°/3 mm.; *ethyl undecylmalonate*, $C_{11}H_{23}\cdot CH(CO_2Et)_2$, b. p. 208—209°/21 mm. (corr.); *undecylmalonic acid*, $C_{11}H_{23}\cdot CH(CO_2H)_2$, m. p. 108·5° (corr.) after recrystallisation from a mixture of acetone and light petroleum.

Tetracosanic acid, $C_{24}H_{48}O_2$, was prepared by heating *docosylmalonic acid* $C_{22}H_{45}\cdot CH(CO_2H)_2$, which was obtained in a somewhat impure state by the saponification of its *ethyl* ester,

$$C_{22}H_{45}\cdot CH(CO_2Et)_2,$$

m. p 48°. The tetracosanic acid thus obtained was purified by conversion into its ethyl ester, $C_{23}H_{47}\cdot CO_2Et$, m. p. 56—57° (corr.), b. p. 118°/0·6 mm. It crystallises in scales from toluene, which have m. p. 87·5—88°. S. B. S.

Cyanopropylallylacetic Acid. [α-Cyano-α-allyl-*n*-valeric Acid]. EMIL FISCHER and WALTER BRIEGER (*Ber.*, 1915, **48**, 1517—1531).—In extension of the re-investigation of the equivalence of the four valencies of carbon (compare Fischer, Rohde, and Brauns, A., 1914, i, 247) which has become necessary in view of the possibility of some change, such as the Walden rearrangement, in the earlier proofs, the behaviour of *d*-α-cyano-α-allylvaleric acid on reduction has been examined. The inactivity of the produced α-cyano-α-propylvaleric acid demonstrates the equivalence of the two alkyl groups.

Ethyl α-cyanovalerate, b. p. 105—110°/15 mm., 222—223° (corr.)/755 mm., reacts with allyl iodide in the presence of sodium ethoxide, forming *ethyl α-cyano-α-allylvalerate*,

$$CH_2{:}CH\cdot CH_2\cdot CPr(CN)\cdot CO_2Et,$$

a colourless oil, b. p. 125—130°/15—20 mm., 241—242° (corr.)/752 mm., from which *α-cyano-α-allylvaleric acid*, a colourless, viscid oil, b. p. 129—130°/0·15 mm., D_4^{18} 1·102, solidifying to needles, m. p. 25—35°, was obtained by hydrolysis with potassium hydroxide; *lead* salt, sparingly soluble needles; *ammonium* salt, needles; *silver* salt, needles; *calcium* salt, crystalline. Recrystallisation of the *brucine* salt gave the *d*-constituent of the acid as the less soluble fraction, whilst with cinchonine the salt of the *l*-acid is less soluble. *d*-Cyano-α-allylvaleric acid was obtained pure by successive recrystallisation as the brucine and morphine salts; it forms colourless, microscopic needles, m. p. 42° (corr.), and has

$[\alpha]_D^{21}+18\cdot22°$ (in neutralised aqueous solution), $[\alpha]_D^{22}+7\cdot97°$ (in acetic acid); the *l*-enantiomorph was also isolated, but in a rather less pure condition. Reduction of the dextro-acid in acetic acid or in alkaline solution by means of hydrogen and platinum black gave inactive *α-cyano-α-propylvaleric acid*, identical with a sample, m. p. 33—34°, D_4^{18} 0·988 in fluid state (hydrate with $1H_2O$, rhombic or hexagonal tablets, m. p. 49—50°), which was obtained by hydrolysis of the corresponding ethyl ester (compare Conrad and Zart, A., 1905, i, 754); *ammonium* salt, needles; *silver* salt, crystalline.

In an attempt to hydrolyse the nitrile group in *dl*-cyanoallylvaleric acid to the carboxylamido-group by heating with sulphuric acid, it was found that the allyl radicle also was affected, the product being the *lactone* of *propylhydroxypropylmalonamic acid*, $NH_2\cdot CO\cdot CPr<\substack{C_3H_6\\ -CO-}>O$, hexagonal plates, m. p. 96—97°; hydrolysis of this compound with sodium hydroxide affected both the lactonic and the amide groups, giving rise to an oily substance, probably the *lactone* of *propylhydroxypropylmalonic acid*; *calcium* salt, crystals with $2H_2O$. When treated in warm sodium carbonate solution with potassium permanganate, *dl*-cyanoallylvaleric acid is oxidised to a dibasic acid, probably dl-*α-cyano-α-propylsuccinic acid*, $CN\cdot CPr(CO_2H)\cdot CH_2\cdot CO_2H$, a crystalline powder, m. p. 123° (corr. decomp.); *calcium* salt, crystalline. Under similar conditions, *d*-cyanoallylvaleric acid underwent oxidation to the corresponding *d*-acid, needles or prisms, m. p. 123° (corr. decomp.), $[\alpha]_D^{18}-32\cdot0°$ (in water). D. F. T.

Preparation and Properties of Hydracrylic Esters. W. A. Drushel and W. H. T. Holden (*Amer. J. Sci.*, 1915, [iv], **40**, 511—514).—Hydracrylic acid was prepared from sodium hydracrylate (A., 1915, i, 54) by treatment with slightly less than the theoretical amount of sulphuric acid (1 in 1), evaporating to dryness, and extracting with absolute alcohol. It was esterified directly by boiling its alcoholic solution with a slight excess of anhydrous copper sulphate free from sulphur trioxide, and yields of 80—90% were obtained. The esters were distilled off under reduced pressure; they boil and decompose under atmospheric pressures. The methyl, ethyl, propyl, and *iso*propyl esters are soluble in water in all proportions. Tables are appended showing the densities at 0° and 25°, the boiling points at various pressures, and the refractive indices of the esters examined, from which the following data are selected: methyl ester, D_4^{25} 1·118, b. p. 79°/12 mm., n_D^{23} 1·4306; ethyl ester, D_4^{25} 1·064, b. p. 84°/12 mm., n_D^{23} 1·4271; *iso*propyl ester, D_4^{25} 1·058, b. p. 95°/12 mm., n_D^{23} 1·4303; propyl ester, D_4^{25} 1·043, b. p. 98°/12 mm., n_D^{23} 1·4341; *iso*butyl ester, D_4^{25} 1·003, b. p. 104°/15 mm., n_D^{23} 1·4342; *iso*amyl ester, D_4^{25} 0·976, b. p. 124°/20 mm., n_D^{23} 1·4374. G. F. M.

The Keto-Enol Equilibria of Oxalacetic Acid, its Esters and Salts. A. Hantzsch (*Ber.*, 1915, **48**, 1407—1422).—The author has extended to oxalacetic acid and its compounds the method of

examination to which he has earlier submitted ethyl acetoacetate (A., 1910, i, 811; 1911, i, 602), and has obtained results which, by comparison with the results of Meyer (A., 1912, i, 940), demonstrate the superiority of the spectrochemical method to the bromine method for the investigation of keto-enol equilibria.

The absorption spectra of the methyl and ethyl esters of oxalacetic acid resemble that of ethyl acetoacetate in variability according to the solvent, the variation being due to a readjustment of the equilibrium between the keto and enol forms; the solutions in ether and light petroleum give an absorption curve approaching that of ethyl ethoxyfumarate, and so contain the enol form almost exclusively; solutions in ethyl alcohol, methyl alcohol, and water progressively show absorptions more divergent from that of ethyl ethoxyfumarate and gradually approaching those of the ethyl esters of dimethyl- and diethyl-oxalacetic acids, a solution in dilute hydrochloric acid, indeed, containing almost entirely the keto-modification.

The sodium salts of the dimethyl and diethyl esters in sodium carbonate solution exhibit absorption spectra closely resembling that of the enol form of the free esters, but with the head of the band at a greater wave-length. Free oxalacetic acid behaves similarly to its esters, showing marked differences in the absorption in different solvents, ranging from almost entirely the enolic form in ether to almost entirely the ketonic form in dilute hydrochloric acid; the results indicate that in this case with aqueous solutions the "bromine" method gives a misleading result. With excess of alkali, oxalacetic acid can behave even as a tribasic acid, the existence of the salts in solution being easily detectable by spectrochemical means, and, indeed, the barium salt, $(C_4HO_5)_2Ba_3$, can be precipitated from the solution of the sodium salt by barium hydroxide solution. The trisodium salt in absorption closely resembles the sodium salt of the dimethyl ester, whilst the mono- and di-sodium salts exhibit almost identical spectra analogous to that of free oxalacetic acid; the trisodium salt is therefore derived from the enol structure, whereas the mono- and di-sodium salts are ketonic to the extent of 98—99%.

The two forms of oxalacetic acid (Wohl and Oesterlin, A., 1901, i, 365) appeared to give solutions of identical optical properties even in ether at $-80°$; a desire to compare the ordinary form of the methyl ester with the form described by Michael and Murphy (A., 1906, i, 179) could not be satisfied on account of failure to prepare the latter.

A comparison of the absorption spectra of maleic and fumaric acids, which are similar, with those of the enolic form of oxalacetic acid (hydroxyfumaric acid) and with dihydroxyfumaric (or dihydroxymaleic) acid shows that the introduction of the first hydroxyl group is of marked effect, whilst the second produces but little further alteration. This is attributed to the formation of a "conjugated" cyclic structure, for example, $\begin{array}{l}\mathrm{C(OH)\cdot CH} \\ \| \\ \mathrm{O\cdots\cdots OH}\end{array}\!\!>\mathrm{C\cdot CO_2H}$

from the enolic compounds, the given structure referring to the cyclic derivative of the enolic form of oxalacetic acid.

D. F. T.

Polarimetric Measurements of Certain Complex Uranyl Salts. A. MAZZUCCHELLI and G. SABATINI (*Gazzetta*, 1915, **45**, ii, 225—250).—The authors have measured at about 15° and 30°, and for lights of four different wave-lengths, the rotatory powers of uranyl tartrate and quinate, both alone and in presence of ammonia or pyridine; similar measurements were made with uranyl malate in presence of ammonia. The results obtained indicate that no complex additive products, but only salts similar to those obtained with fixed alkalis, are formed. The variations produced in the rotatory power of uranyl tartrate by addition of different proportions of potassium hydroxide are related to the formation of mono- and di-basic salts. The conclusion is drawn that the complex uranylotartaric anion is possessed of little stability.

T. H. P.

The Preparation of β-Sulphidodibutyric Acid. HELMUTH SCHEIBLER (*Ber.*, 1915, **48**, 1443—1444. Compare Lovén and Johansson, A., 1915, i, 866).—β-Chlorobutyric acid can be obtained in almost quantitative yield by saturating an ethereal solution of crotonic acid with hydrogen chloride and keeping it at the ordinary temperature for three days. This acid is neutralised and the aqueous solution, mixed with potassium sulphide, kept for three days at 37°, when a mixture of the isomeric β-sulphidodibutyric acids, together with some β-thiolbutyric acid, is produced. Sodium sulphide cannot be used in place of the potassium salt, as the product is then crotonic acid.

Ethyl *l*-di-β-hydroxybutyrate, b. p. 145°/12 mm., can be obtained by heating methyl crotonate (1 mol.) and ethyl *l*-β-hydroxybutyrate (1 mol.) with potassium (0·1 at.) for five hours at 120°.

D. F. T.

Unsaturated Sulphidodicarboxylic Acids. I. β-Sulphidodicrotonic Acid. HELMUTH SCHEIBLER and WALTHER BUBE (*Ber.*, 1915, **48**, 1445—1461).—Ethyl β-chloro*iso*crotonate, b. p. 158°, reacts readily with potassium sulphide in alcoholic solution, yielding *ethyl β-sulphidodicrotonate*, a heavy, yellow oil, b. p. 150—153°/4 mm.; the same product is obtained with the stereoisomeric ethyl β-chlorocrotonate, but the reaction in this case is decidedly less rapid, so that the structure $\begin{array}{ccc} H\cdot C\cdot CO_2Et & & CO_2Et\cdot CH \\ \| & & \| \\ CMe & —S— & CMe \end{array}$ is assumed for the product, this view being confirmed by the existence of an anhydride of the corresponding acid. In the preparation of this ester, *ethyl β-thiolcrotonate*, $SH\cdot CMe{:}CH\cdot CO_2Et$, is obtained as a by-product, a somewhat more satisfactory procedure for its production being to treat ethyl β-chlorocrotonate with potassium hydrogen sulphide; *copper* derivative, $C_6H_9O_2SCu$, yellow, amorphous solid.

By cautious hydrolysis of ethyl β-sulphidodicrotonate with alcoholic potassium hydroxide at the ordinary temperature, it is possible to obtain *ethyl hydrogen β-sulphidodicrotonate*, prisms, m. p. 104—105°, decomp. at 210° with formation of carbon dioxide. More energetic hydrolysis of the ethyl ester gives *β-sulphidodicrotonic acid*, $S(CMe{:}CH{\cdot}CO_2H)_2$, needles or prisms, m. p. 212—215° with decomposition into carbon dioxide and a volatile oil of unpleasant odour, possibly the unsaturated *sulphide*, $S(CMe{:}CH_2)_2$; *silver* salt ($1H_2O$), colourless; *copper* salt, green; *lead* salt, colourless; *ferric* salt, yellowish-red; *barium* salt ($1H_2O$), irregular tablets. The *methyl* ester, obtained by heating β-sulphidodicrotonic acid with alcohol and a little sulphuric acid, is a pale yellow oil, b. p. 116—117°/0·6 mm., which on solidification gives prisms, m. p. 23·5°. *β-Sulphidodicrotonamide*, rhombic prisms, m. p. 192°, can be prepared from the acid by first treating with phosphorus trichloride and submitting the oily acid *chloride* to the action of ammonia. When the acid is heated for a short time with acetic anhydride, it undergoes dehydration to the corresponding acid *anhydride*, an undistillable oil.

The hydrogen atoms of the methine groups are remarkably active, being replaceable by halogen elements and also by alkali metals. Thus, with sulphuryl chloride (used instead of chlorine, as being less likely to affect the ethylenic linkings) in ethereal solution, ethyl β-sulphidodicrotonate is converted into *ethyl $\alpha\alpha$-dichloro-β-sulphidodicrotonate*, $S(CMe{:}CCl{\cdot}CO_2Et)_2$, a deep yellow, viscous oil of pleasant odour, b. p. 158—160°/0·1 mm. (slight decomp.), which is slowly decomposed by water or alcohol with liberation of the chlorine. Ethyl β-sulphidodicrotonate reacts with the alkali metals with liberation of hydrogen, but the *disodium* derivative, $S(CMe{:}CNa{\cdot}CO_2Et)_2$, is best prepared by mixing the ester with an alcoholic-ethereal solution of sodium ethoxide in an atmosphere of hydrogen, the product being obtained as a yellowish-red powder, which regenerates the ester on the addition of water. Treatment of the disodium compound with such reagents as phosphoryl chloride, sulphur chloride, acetaldehyde, and iodine failed to give any satisfactory results, possibly due, in part at least, to steric hindrance. The only indication of condensation to a cyclic compound was observed with β-sulphidodicrotonic acid itself, which when warmed with sulphuric acid gives rise, among oily products, to needles of a substance of feeble basic properties, which may be *dimethylthiopyrone*, $S{<}{\substack{CMe{:}CH\\CMe{:}CH}}{>}CO$.

Methyl β-sulphido-$\alpha\alpha$-dimethyldicrotonate, $S(CMe{:}CMe{\cdot}CO_2Me)_2$, obtained by the interaction of ethyl β-chloro-α-methylcrotonate and potassium sulphide in methyl-alcoholic solution is a pale yellow oil, b. p. 149—150°/5 mm. The corresponding *β-sulphido-$\alpha\alpha$-dimethyldicrotonic acid*, $S(CMe{:}CMe{\cdot}CO_2H)_2$, forms microscopic, compact crystals, m. p. 181° (decomp.); it was obtained as a by-product in the preparation of the ester, owing to the hydrolytic effect of the potassium sulphide. D. F. T.

Catalytic Reduction. IX. The Catalytic Reduction of Aldehydes and Ketones. A. SKITA [with P. STUCKART] (*Ber.*, 1915, **48** 1486—1498. Compare Ipatiev, A., 1913, i, 10).—Contrary to the belief of Ipatiev, α-methyl-β-ethylacraldehyde can be reduced by hydrogen at the ordinary temperature when working with an aqueous alcoholic solution to which palladium chloride and gum arabic have been added, and with an additional pressure of one atmosphere; the reaction product contains α-methyl-*n*-valeraldehyde and β-methyl-Δ^{β}-pentenyl alcohol in the proportions 9:1, this result being similar to that obtained earlier in the reduction of acraldehyde (A., 1913, i, 63). When reduction is effected in aqueous acetic acid solution in the presence of colloidal platinum for such a time that a bimolecular proportion of hydrogen is absorbed, α-methyl-β-ethylacraldehyde is converted quantitatively into β-methyl-*n*-amyl alcohol, which compound Ipatiev has incorrectly described as γ-methyl-*n*-amyl alcohol (*loc. cit.*).

Mesityl oxide can be easily reduced in aqueous solution by colloidal platinum and hydrogen, the product being δ-keto-β-methyl-*n*-pentane, the same substance having been obtained earlier by Ipatiev in the reduction with colloidal palladium and hydrogen at high temperature and pressure. In acetic acid solution, acetylacetone is reduced to methylpropylcarbinol and mesityl oxide to methyl*iso*butylcarbinol.

Exhaustive hydrogenation of acetone, methyl propyl ketone, diethyl ketone, and pulegone in aqueous acetic acid containing colloidal platinum led only to the formation of the corresponding secondary alcohols. Phenylacetaldehyde under similar conditions gave rise to phenylethyl alcohol accompanied by a small quantity of ethylbenzene, and *cyclo*hexanone yielded *cyclo*hexanol with a little *cyclo*hexane. Hydrogenation of benzaldehyde in a similar manner led, through benzyl alcohol, to the production of toluene and methyl*cyclo*hexane, whilst with benzophenone at 60° *di*cyclo*hexylmethane*, $CH_2(C_6H_{11})_2$, b. p. 248—250°/750 mm., was obtained.

When reduced in the general manner in acetic acid solution, α- and β-ionone yielded 1:1:3-*trimethyl*-2-γ-*hydroxy*-n-*butyl*cyclo*hexane*, a liquid b. p. 142—143°/20 mm., D^{20} 0·9126, with an odour resembling that of cedar wood; *acetate*, b. p. 131°/11 mm.

D. F. T.

Production of Alkali Metal Derivatives of Ketones with a View to the Preparation of Alcohols. FARBENFABRIK VORM. F. BAEYER & Co. (*Fr. Pat.* 474745; from *J. Soc. Chem. Ind.*, 1915, **34**, 1116).—Alkali metal derivatives of ketones are obtained by the action of alkali metals or their amides on ketones at temperatures below 0°. Thus at −15° to −20° sodioacetone $CH_3{\cdot}C(ONa){:}CH_2$, is formed as a colourless, crystalline powder by adding anhydrous acetone (58 parts) to sodamide (40 parts) in 600 parts of anhydrous ether. These compounds react with acetylene and similar compounds to form alcohols. The production of the alcohol may be carried out in one operation by allowing, for example, acetylene to react with a mixture of acetone with sodium,

sodamide, or sodium ethoxide, or acetone to react with sodium acetylide, $NaHC_2$, or sodium carbide, when γ-methylbutinenol, $OH{\cdot}CMe_2{\cdot}C{:}CH$, is formed. This on reduction gives γ-methylbutenol, $OH{\cdot}CMe_2{\cdot}CH{:}CH_2$. Similarly, γ-methylpentinenol and γ-methylpentenol may be prepared from methyl ethyl ketone.

G. F. M.

Hexabromodiacetyl. C. LORING JACKSON and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1915, **37**, 2522—2536).—The compound described as having the formula $CBr_3{\cdot}CHBr{\cdot}CO{\cdot}CO{\cdot}CBr_3$ (Jackson and Fiske, A., 1914, i, 296) is in reality *hexabromodiacetyl*, $CBr_3{\cdot}CO{\cdot}CO{\cdot}CBr_3$, the m. p. being 100—101° instead of 97—98° as previously stated. The m. p.'s of the hemiacetals produced by the action of cold methyl or ethyl alcohol are 105° and 96—97° respectively instead of 100—101° and 93—94° as reported earlier; the hexabromodiacetylmonomethylhemiacetal obtained with the former alcohol crystallises in long needles, short prisms, and apparently tetragonal octahedra, all of the same m. p. The product obtained by the action of benzyl alcohol on hexabromodiacetyl is probably *pentabromodiacetylmonobenzylhemiacetal*,

$$CHBr_2{\cdot}CO{\cdot}C(OH)(O{\cdot}CH_2Ph){\cdot}CBr_3;$$

m-nitrobenzyl alcohol does not combine with hexabromodiacetyl.

Hydriodic acid or acetone at the ordinary temperature reduces hexabromodiacetyl to tetrabromodiacetyl, whilst with a mixture of alcohol and acetone *pentabromodiacetylmonoethylhemiacetal*, $CHBr_2{\cdot}CO{\cdot}C(OH)(OEt){\cdot}CBr_3$, prisms, m. p. 115°, is obtained. Hexabromodiacetyl reacts with an aqueous solution of potassium iodide, giving a substance which is probably *bromotri-iodoacetone*, $CI_3{\cdot}CO{\cdot}CH_2Br$, lemon yellow needles, decomp. at 122—125°.

The substance, m. p. 71—72°, described in the previous paper (*loc. cit.*) as obtained by the action of water on hexabromodiacetyl, and also obtained as a by-product in the preparation of this substance, is pentabromoacetone. D. F. T.

Formation and Preparation of Glucosemonoacetone. JAMES COLQUHOUN IRVINE and JAMES LESLIE AULD MACDONALD (T., 1915, **107**, 1701—1710).—As the acetone derivatives of polyhydroxy-compounds are very useful in the preparation of partially acylated products (compare Fischer, A., 1915, i, 118), the somewhat elusive mono-acetone compounds need to be rendered readily available. Glucosemonoacetone has long been regarded as an intermediate product in the formation of glucosediacetone, but attempts to prepare the substance, bearing this in mind, have frequently given such contradictory results (compare T., 1913, **103**, 1896) that the authors have come to the conclusion that the diacetone compound is the primary product, and that any of the mono-derivative which may arise is the result of some adventitious partial hydrolysis.

The best way to prepare glucosemonoacetone, therefore, consists in the partial hydrolysis of the diacetone. This compound is completely hydrolysed by 0·1% hydrochloric acid at 50°, but loses only one residue at 30°. The hydrolysis is stopped when the lævorota-

tion of the solution no longer diminishes, and then the acid is neutralised by silver carbonate and the filtrate is evaporated. The residue is crystallised from hot ethyl acetate, which deposits the glucosemonoacetone on cooling, leaving a substance in the mother liquor which proves to be a solid solution of the diacetone in the monoacetone compound. The latter can be separated into the constituents by fractional crystallisation from water.

It is found that analytically pure glucosemonoacetone may vary most unaccountably in rotation and m. p. The strictest test of purity is afforded by hydrolysis with 0·1% hydrochloric acid at 75°, for the permanent specific rotation, calculated for the glucose formed, should not exceed +52·5°.

The original intention in preparing large quantities of glucosemonoacetone was to convert the compound into trimethyl glucose and ultimately into glucosamine (T., 1913, **103**, 564). On this occasion the crude trimethyl glucose was distilled, b. p. 153°/0·15 mm., but the distillate was found to be $\gamma\epsilon\zeta$-trimethylglucosone.

J. C. W.

The Configuration of some of the Higher Monosaccharides. GEORGE PIERCE (*J. Biol. Chem.*, 1915, **23**, 327—337).—Of the nonoses synthesised up to the present, only the mannononose has been found to ferment with yeast. Attempts are being made to determine the configuration of this substance, and the author has succeeded in determining that of the following sugars with more than six carbon atoms: α- and β-galoheptose, α- and β-mannoheptose, and $\alpha\alpha$- and $\beta\alpha$-manno-octose. The two heptitols derived from *d*-mannose have the constitutions I and II, whereas those derived from *d*-galactose have the formulæ III and IV.

CH_2OH	CH_2OH	CH_2OH	CH_2OH
HCOH	HOCH	HCOH	HOCH
HOCH	HOCH	HCOH	HCOH
HOCH	HOCH	HOCH	HOCH
HCOH	HCOH	HOCH	HOCH
HCOH	HCOH	HCOH	HCOH
CH_2OH	CH_2OH	CH_2OH	CH_2OH
(I.)	(II.)	(III.)	(IV.)

Formulæ I and III are optical antipodes. It has been found that *d*-α-mannoheptitol combines with *d*-α-galaheptitol to form a compound with table-like crystals with m. p. 205° (corr.), and this fact, together with the known physical properties (m. p. and optical rotation), indicates that these alcohols are optical antipodes. Formulæ I and III must therefore be assigned to the α-compounds, leaving II and IV for the β-compounds.

It has also been found that the dibasic acid derived from the oxidation of *d*-α-mannoheptose, and called by the author *mannoheptaric acid*, has the same m. p. as the corresponding *d*-α-galaheptaric acid, but the opposite rotation. Hence the two acids are

antipodes. On oxidising *d*-*aa*-manno-octonic acid with nitric acid, a double lactose of the dibasic (*octaric*) acid is obtained, which appears to be optically inactive. The two possible configurations of this dibasic acid are:

```
     H H                              H H  H
   H H O O H H                      H H O O H O
CO2H·C·C·C·C·C·C·CO2H   and   CO2H·C·C·C·C·C·C·CO2H
   O O H H O O                      O O H H O H
   H H   H H                        H H    H
      (V.)                              (VI.)
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As V is inactive, this must represent the formula of *aa*-manno-octaric acid.

By the action of hydrogen cyanide on *d*-mannose, the author has succeeded in obtaining, in addition to the acid prepared by E. Fischer, an isomeric acid, designated as *β-mannoheptonic acid.* The two isomerides are convertible one into the other by heating with pyridine at 137—142°. The *β*-acid was separated from the mother liquors after the preparation of the barium and cadmium salts of the *a*-acid in the form of a *phenylhydrazide*, $C_{13}H_{20}O_7N_2$, m. p. 190°, $[a]_D^{27}$ −25·8, after recrystallisation from 70% alcohol. By reducing the *d*-*β*-mannoheptonic acid in the form of its lactone with sodium amalgam, a heptose was obtained of which the osazone melted at 210°. The p-*nitrophenylhydrazone*, $C_{13}H_{19}O_8N_3$, obtained from this sugar softens at 190°, melts at 198°, and decomposes at 203°. On treatment with benzaldehyde it yields the free sugar, d-*β-mannoheptose.* On reduction with sodium amalgam this sugar yields d-*β-mannoheptitol*, m. p. 217°, after softening at 150—153°.

d-*β*-Galaheptitol was also prepared by the reduction of crude *d*-*β*-galaheptose with sodium amalgam. This sugar, $C_7H_{16}O_7$, softens at 138° and melts at 141—144°.

d-*a*-Mannoheptaric acid prepared according to E. Fischer's directions had m. p. 168° and $[a]_D^{20}$ after eighteen hours = −16·5° and after forty-eight hours = −17·9°, and appears to be the optical antipode of *d*-*a*-galaheptaric acid.

The preparation of the double *lactone* of d-*aa-mono-octaric acid*, $C_8H_{10}O_8$, by the oxidation of *d*-*aa*-manno-octonic acid lactone with nitric acid is also described. This lactone decomposes without melting, and is only slightly soluble in water. Its solution in sodium hydroxide solution is, as already stated, apparently optically inactive. S. B. S.

Preparation of Glycine and Ethyl Carbonate. W. A. DRUSHEL and D. R. KNAPP (*Amer. J. Sci.*, 1915, [iv], **40**, 509—510).—An attempt was made to increase the yield of aminoacetic acid from chloroacetic acid by allowing the latter to react at 0° with a solution of ammonia kept saturated by passing in gaseous ammonia during the reaction, which required at this temperature about five days for completion. The yield, however, in no case exceeded 55% of the theoretical, and this result can be attained less laboriously by Kraut's method, working at 10°. The velocity-

constant at 0° was 0·000223. A modification of Neff's method for the preparation of cyanoformic ester from chloroformic ester (A., 1896, i, 74) by substituting an absolute alcoholic solution of potassium cyanide for an aqueous alcoholic solution, and working at ordinary temperatures at first, and finally boiling for an hour under reflux, only resulted in the formation of ethyl carbonate in 50% yield. No cyanoformic ester could be detected in the reaction mixture.
G. F. M.

The Mutual Relationship of the Optically Active Forms of ββ'-Iminodibutyric Acid and β-Aminobutyric Acid. II. HELMUTH SCHEIBLER and J. MAGASANIK (*Ber.*, 1915, **48**, 1810—1815. Compare Scheibler, A., 1912, i, 682).—*meso*-ββ'-Iminodibutyric acid, previously described as an oil, has now been obtained in the form of a crystalline solid, m. p. 177—178° (corr., decomp.); this is two degrees lower than the m. p. of the active forms, but considerably higher than that of the racemic acid, which is probably a mixture. *Methyl* meso-*ββ'-iminodibutyrate* is an oil, b. p. 130°/10 mm., which is converted by methyl iodide into *methyl ββ'-methyliminodibutyrate*; this was isolated by treatment with benzyl iodide, the product being *benzylmethyl-γγ'-dicarbomethoxydi*iso*propylammonium iodide*, $CH_2Ph·N(CHMe·CH_2·CO_2Me)_2MeI$, a crystalline solid which was accompanied by a syrupy oil, possibly consisting of a stereoisomeride.

β-Methylaminobutyric acid, a crystalline solid, can be obtained by the direct addition of methylamine to crotonic acid at 140°, and also by the action of an alcoholic methylamine solution on β-chlorobutyric acid at 100°; the yield by the latter method is poor on account of the concurrent formation of succinic acid, whilst if the reaction is effected in aqueous solution, β-hydroxybutyramide is almost exclusively obtained.

dl-β-Chlorobutyric acid can be resolved by recrystallisation of the quinine salt from water, the *l*-acid forming the more sparingly soluble salt; the *laevo*-acid crystallised in needles, $[\alpha]_D -33·4°$, whilst the pure *dextro*-acid, separated from the mother liquors and purified as its sparingly soluble brucine salt, had $[\alpha]_D +46·6°$.
D. F. T.

New Synthesis of Amido-oxalylbiuret and Certain Derivatives of Oxalic Acid. J. TH. BORNWATER (*Rec. trav. chim.*, 1915, **35**, 124—129).—Carbethoxyethoxalylcarbamide,

$$CO_2Et·NH·CO·NH·CO·CO_2Et,$$

is readily obtained by the action of ethoxalyl chloride on ethyl allophanate in boiling benzene solution; it is transformed into amido-oxalylbiuret by ammonia (compare A., 1913, i, 1309).

The action of hot solutions of oxalyl chloride in benzene on amides and amines has been further studied (compare A., 1911, i, 617). In some cases derivatives of oxalic acid are produced, whilst in others loss of a carbonyl group occurs and derivatives of carbamide are formed; at present it is not possible to predict the course of the reaction. The following compounds are described: *oxalyldi-*

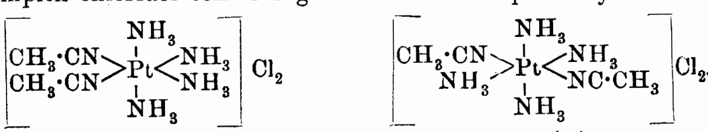
α-aminobutyric diethyl ester, $C_2O_2[NH·CH(CO_2Et)·CH_2Me]_2$, m. p. 63—64°; *oxalyldi*-n-*butyramide*, $C_2O_2(NH·CO·CH_2·CH_2Me)_2$, colourless needles, m. p. 197°; *oxalyldi*-n-*butyranilide*, m. p. 156°.

Oxalyl chloride converts malonamide into barbituric acid, but does not attack succinamide. H. W.

Two Series of Complex Derivatives of Bivalent Platinum, Corresponding with the Index of Co-ordination 6. L. Tschugaev and W. Lebedinski (*Compt. rend.*, 1915, **161**, 563—564).—An account of two derivatives of bivalent platinum belonging to the type $(Pt6A)X_2$. Platinous chloride bisacetonitrile, prepared by Hofmann and Bugge from acetonitrile and potassium platinochloride (compare A., 1907, i, 489), on carefully warming is converted into an isomeride, the two forms being referred to respectively as α and β. Both these isomerides fix four molecules of ammonia when boiled with aqueous ammonia, or by the action of liquid ammonia in sealed tubes. The two isomeric *chlorides*, $[Pt2CH_3·CN,4NH_3]Cl_2$, are thus obtained as colourless substances, very soluble in water, the chlorine being completely ionised in solution. They both yield *platinochlorides*,

$$[Pt2CH_3·CN,4NH_3],PtCl_4,$$

and *picrates*, $[Pt2CH_3·CN,4NH_3](C_6H_3O_7N_3)_2$. The ammonia is very strongly combined in the molecule. It cannot be titrated with mineral acids, and is only removed on boiling with hydrochloric acid, 2 mols. of ammonia and 2 mols. of acetonitrile being eliminated, the α-form giving Peyrone's chloride and the β-form the chloride of Reiset's base II. The formulæ assigned to the two complex chlorides containing ammonia are respectively



(α.) (β.)

W. G.

Constitution of α-Amino-acids. Conductivity of Iminodiazoacetic Acid and its Monosodium Salt. H. J. Backer (*Chem. Weekblad*, 1915, **12**, 943—946).—From the results of determinations of the molecular electrical conductivity of iminodiazoacetic acid, the author has come to the conclusion that the structure of the free acid corresponds with the formula

$$\begin{array}{l} CH_2·NH·CH_2·CO_2H. \\ | \quad\;\; \vdots \\ CO_2\text{-}H \end{array}$$

The monosodium salt is to be regarded as derived from this acid, its unsubstituted carboxyl group being linked to the amino-group of the same molecule. A. J. W.

The Thermal Decomposition of Hydrogenated Aromatic Hydrocarbons. David Trevor Jones (T., 1915, **107**, 1582—1588).—When heated in contact with porous porcelain, the temperature being raised slowly, *cyclo*hexane, methyl*cyclo*hexane, and tetra-

hydronaphthalene all begin to decompose between 490° and 510°, whilst dihydronaphthalene decomposes at about 390°. Having regard to the comparatively low temperatures of decomposition, the proportion of hydrogen in the resulting gases (about 40% for the *cyclo*hexanes and 80% for the hydrogenated naphthalenes) is remarkably high. In view of the fact that with paraffins, which contain more than two carbon atoms, scission takes place between carbon and carbon, it is evident that there is a fundamental difference between the *cyclo*hexanes and the paraffins in so far as the stability of the carbon–hydrogen linkings is concerned. It seems probable that the *cyclo*hexane first loses two atoms of hydrogen, yielding *cyclo*hexene, which then decomposes in two ways, producing on the one hand benzene and hydrogen, and on the other butadiene and ethylene. H. M. D.

The Benzene Nucleus. ANÍBAL CHACÓN (*Anal. Soc. Quim. Argentina*, 1915, **3**, 32—43, 155—166).—A theoretical paper in which the author summarises the various theories as to the structure of benzene, and amplifies the views set forth by him in his pamphlet "The Cyclic Molecule." A. J. W.

Replacement of Substituents in the Benzene Nucleus. A. F. HOLLEMAN (*Rec. trav. chim.*, 1915, **35**, 1—66).—As complement to his researches on the introduction of substituents into the benzene nucleus, the author has commenced an investigation on their replacement.

[With W. J. DE MOOY.]—The action of a methyl-alcoholic solution of sodium methoxide and of diethylamine on the six isomeric dichloronitrobenzenes and the dichloro- and chloronitro-benzenes has been studied.

The isomeric 2:5-, 3:4-, 2:6-, and 2:3-dichloronitrobenzenes react with sodium methoxide at 85°, one of the chlorine atoms being replaced by the methoxy-group (6-*chloro*-2-*nitro*-1-*methoxybenzene* has m. p. 54·5°); in the case of the 2:4-isomeride, replacement of both chlorine atoms is possible, but that which occupies the ortho-position to the nitro-group is first attacked; under similar treatment, the 3:5-isomeride yields a product, m. p. 134—145°, which is possibly a derivative of azoxybenzene, but could not be isolated in the pure state. *o*- and *p*-Chloronitrobenzenes yield the corresponding anisoles, but the meta-derivative is transformed into 3:3′-dichloroazoxybenzene. Protracted heating with methyl alcoholic sodium methoxide at 180° converts the dichlorobenzenes into the isomeric chlorophenols. The reaction has been quantitatively investigated at 25°, 50°, 85°, and 100°, and the results are given in an extended series of tables. The relative velocity of reaction for the different isomerides ($NO_2=1$) is illustrated by the figures within brackets: 1:2:4- (100), 1:2:5- (20·2), 1:3:4- (89·7), 1:2:3- (8·9), 1:2:6- (0·7). 1:2- (1·9), 1:4- (7·2). Among the dichlorobenzenes it is remarkable that the chlorine is most easily replaced in the meta-isomeride.

A closely similar series of experiments has been performed with

diethylamine. In this case the velocities of reaction are much smaller than with sodium methoxide, but increase considerably more rapidly with rise of temperature. When sodium methoxide is used, the velocity constants can be represented as functions of the temperature by means of a formula with two constants.

The following new substances are described: 4-*chloro-2-nitrodiethylaniline*, red needles, m. p. 32°; 3-*chloro-6-nitrodiethylaniline*, reddish-brown needles, m. p. 30·5°; 2-*chloro-5-nitrodiethylaniline*, yellow crystals, m. p. 8·2°; 2-*chloro-6-nitrodiethylaniline*, yellow crystals, m. p. 9°; 3-*chloro-2-nitrodiethylaniline*, pale yellow crystals, m. p. 44°; *o-nitrodiethylaniline*, m. p. −37°. *m*-Chloronitrobenzene and the three dichlorobenzenes do not react with diethylamine at 110° for six days or at 180° for five hours.

[With J. TER WEEL.]—The action of methyl-alcoholic solutions of sodium methoxide and ammonia on the six isomeric chlorodinitrobenzenes has been investigated.

In the cases of the 3:1:2-, 2:1:4-, and 4:1:2-isomerides, the nitro-group in the position 1 in each case suffers replacement under the action of sodium methoxide or ammonia; with the 4:1:3- and 2:1:3-isomerides, on the other hand, the chlorine atom is replaced. The 1:3:5-isomeride, however, does not undergo a corresponding alteration.

Quantitatively, the reactions have been studied at 25° and 0° respectively, since, at higher temperatures, the change proceeds with inconvenient rapidity. The results are given in an extensive series of tables. Generally, it is noticeable that the velocities of the reactions are much greater with sodium methoxide than with ammonia, and, further, that the order of velocities is not the same for each reagent. The presence of a nitro-group in the ortho- or para-position to a chlorine atom facilitates the replacement of the latter, whilst a nitro-group in the meta-position has the opposite effect; similarly, a nitro-group is found to be mobile when in the ortho- or para-position to a second nitro-group. H. W.

Crystalline Form of α-Trinitrotoluene. E. ARTINI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 274—279).—According to Friedländer (*Zeitsch. Kryst. Min.*, 1879, **3**, 168), 2:4:6-trinitrotoluene crystallises in the rhombic system [$a:b:c=0·7586:1:0·5970$]. The author finds, however, that the crystals are only pseudorhombic, and belong to the prismatic class of the monoclinic system,

$$[a:b:c=1·64047:1:0·61936;\ \beta=89°29'9'']$$;

D 1·654. The optical and morphological data are given in detail. The analogy of this crystalline form with that of rhombic 1:3:5-trinitrobenzene (compare Groth, *Chem. Krystallographie*, IV) is indicated. T. H. P.

Dynamic Researches on Friedel and Craft's Reaction. S. C. J. OLIVIER (*Rec. trav. chim.*, 1915, **35**, 109—123. Compare Olivier and Böeseken, A., 1913, ii, 575; Olivier, A., 1914, i, 818).—The author has examined the action of aluminium chloride (1 mol.) on solutions

of certain sulphonic chlorides (1 mol.) and sulphones (1 mol.) in benzene, and is led to the general conclusion that a molecule of aluminium chloride cannot transform more than one molecule of sulphonic chloride. Apparently, the free sulphonic chloride is unable to withdraw aluminium chloride from compounds such as $C_6H_4Br\cdot SO_2Ph,AlCl_3$, and only such compounds as

$$C_6H_4Br\cdot SO_2Cl,AlCl_3$$

react with benzene.

It is further shown that the catalyst is paralysed to an almost equal extent by the different sulphonic chlorides and sulphones. The considerable differences in the velocity constants observed for the different sulphonic chlorides with benzene cannot, therefore, be attributed to an unequal paralysis of the catalyst, but are due to the direct influence of the group which enters the benzene nucleus. The degree of paralysis has been determined approximately.

Additive compounds of the type $R\cdot SO_2Cl,AlCl_3$, which are most readily formed, are most active towards benzene.

m-Nitrodiphenylsulphone forms colourless needles, m. p. 80·5—81° (corr.). H. W.

Colour Dimorphism with Stilbene Derivatives. PAUL PFEIFFER [with S. BRAUDE, J. KLÉBER, G. MARCON, and P. WITTKOP], (*Ber.*, 1915, **48**, 1777—1809).—It has been found that many nitromethoxystilbenes can exist in two forms of different colour, yellow and orange coloured respectively, one generally being stable at the ordinary temperature whilst above 100° the other form is more stable. The one modification changes so readily into the other form on heating that the observed m. p. is always the same for both. Thus *4-nitro-4′-methoxystilbene*,

$$NO_2\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot OMe,$$

prepared by the condensation of *p*-nitrophenylacetic acid with anisaldehyde in the presence of piperidine at 100°, crystallises from hot acetic acid in orange-yellow tablets or leaflets, m. p. 132—134°, whereas, if caused to separate from benzene solution by addition of light petroleum, the substance separates in greenish-yellow needles, which become orange coloured near 100°, and have the same m. p. as the former modification. Similarly, *4-nitro-2-cyano-4′-methoxystilbene*, $NO_2\cdot C_6H_3(CN)\cdot CH{:}CH\cdot C_6H_4\cdot OMe$, obtained by the condensation of *p*-nitro-*o*-toluonitrile and anisaldehyde in the presence of a little piperidine at 140—150°, can exist in two modifications, orange-red leaflets, m. p. 198°, from hot acetic acid, and a yellow powder of the same m. p. produced when a cooled acetic acid solution is poured into water. The isomeric 2-nitro-4-cyano-4′-methoxysilbene crystallises in small, yellow leaflets when a hot solution in benzene or acetic acid is rapidly cooled, whilst on slow evaporation at the ordinary temperature the solutions yield orange-coloured crystals, which are also obtained if the yellow form is kept moistened with benzene; the yellow crystals turn orange-coloured at 120—125°, the common m. p. being 157—158°; both modifica-

tions are converted by bromine into 3-*nitro*-4-($\alpha\beta$-3′:5′-*tetrabromo*-4′-*methoxyphenylethyl*)*benzonitrile*,

$$CN\cdot C_6H_3(NO_2)\cdot CHBr\cdot CHBr\cdot C_6H_2Br_2\cdot OMe,$$

colourless leaflets, m. p. 210—211° (decomp.); a third crystalline form, tablets with $\frac{1}{2}C_6H_6$, is obtained when a benzene solution is allowed to evaporate at about 5°. In like manner, *ethyl* 2-*nitro*-4′-*methoxystilbene*-4-*carboxylate*,

$$CO_2Et\cdot C_6H_3(NO_2)\cdot CH\!:\!CH\cdot C_6H_4\cdot OMe,$$

prepared by the action of alcoholic hydrogen chloride solution on the nitrile, can exist in two forms, yellow needles from hot solvents and orange-coloured tablets stable at the ordinary temperature, both m. p. 103—104°; no change in the colour of the orange form was observable below the m. p., and the solutions of both forms were identical in colour. The corresponding *methyl* ester, obtained in an analogous manner, crystallised first in yellow needles, from which the orange modification was prepared by keeping at 100—105° for some hours and recrystallising from hot alcohol; the m. p. of the latter form is 117—118°, and the yellow modification changes to this form below this temperature. 2-*Nitro*-4′-*methoxystilbene*-4-*carboxylic acid* separates from all solvents in yellow needles or leaflets, m. p. 250°; an orange-coloured modification was only obtainable by heating the *pyridine* salt (yellow needles) at 90—100°, and was found to be converted into the yellow form at 140°; the *potassium* salt, orange leaflets or needles with $2H_2O$, and the *sodium* salt, orange-brown leaflets with $6H_2O$, yellow needles with $5H_2O$, yellow, crystalline powder with $2H_2O$, and an orange-brown powder when anhydrous, were also prepared.

With 2:4-dinitro-4′-methoxystilbene only one modification was isolable, *additive* compounds (prismatic crystals) with $\frac{1}{2}C_6H_6$ and $\frac{1}{2}NH_2Ph$ respectively also having the same orange-red colour. 2-*Nitro*-4-*amino*-4′-*methoxystilbene*,

$$NH_2\cdot C_6H_3(NO_2)\cdot CH\!:\!CH\cdot C_6H_4\cdot OMe,$$

prepared by reduction of the dinitro-compound with ammonium sulphide in alcoholic solution, was also obtained in only one form, red needles, m. p. 154—157°, but its *acetyl* derivative gives a yellow form, needles, and an orange-red form, leaflets, both m. p. 181—182°, whilst the *benzoyl* derivative also exists in a yellow form, leaflets or needles, m. p. 172°, and an orange-red form, of the same m. p., the yellow modification being more stable at the ordinary temperature.

Other compounds prepared during the course of the preceding investigation were the following. allo-2:4-*Dinitrostilbene*,

$$C_6H_3(NO_2)_2\cdot CH\!:\!CHPh,$$

yellow tablets, m. p. 127°, obtained by exposing the ordinary isomeride in xylene solution to ultraviolet light. 2-*Nitro*-4-iso*valerylaminostilbene*, $CHPh\!:\!CH\cdot C_6H_3(NO_2)\cdot NH\cdot CO\cdot CHMeEt$, yellow needles, m. p. 139°, produced by the interaction of the acid chloride and the amino-compound. 4-*Nitro*-4′-*methylstilbene*,

$$NO_2\cdot C_6H_4\cdot CH\!:\!CH\cdot C_6H_4Me,$$

greenish-yellow leaflets, m. p. 150°, from the condensation of *p*-nitrophenylacetic acid and tolualdehyde in the presence of a

little piperidine. 2-*Nitro-4'-methoxystilbene*,

$NO_2 \cdot C_6H_4 \cdot CH{:}CH \cdot C_6H_4 \cdot OMe$,

deep yellow needles, m. p. 89—90°, prepared from 2-nitro-4-amino-4'-methoxystilbene by reduction of its *diazonium sulphate* (red leaflets, decomp. at 165°) with alcohol. 4-*Amino-4'-methoxystilbene*, $NH_2 \cdot C_6H_4 \cdot CH{:}CH \cdot C_6H_4 \cdot OMe$, brownish-yellow leaflets, m. p. 173—174° (*acetyl* derivative, almost colourless leaflets, m. p. 237°; *benzoyl* derivative, almost colourless leaflets, m. p. 249°), obtained by reduction of the corresponding nitromethoxystilbene with stannous chloride. 4-*Nitro-3'-methoxystilbene*, pale yellow leaflets, m. p. 87°, from the condensation of *m*-methoxybenzaldehyde and *p*-nitrophenylacetic acid with a little piperidine at 160°. 4-*Nitro-2'-methoxystilbene*, yellow needles, m. p. 122°, obtained by a similar condensation of salicylaldehyde methyl ether and *p*-nitrophenylacetic acid at 120°. 4-*Nitro-4'-dimethylaminostilbene*,

$NO_2 \cdot C_6H_4 \cdot CH{:}CH \cdot C_6H_4 \cdot NMe_2$,

red leaflets with a bluish glance, m. p. 250—251°, prepared in the general manner. 2-*Nitro-4-cyano-2'-methoxystilbene*,

$NO_2 \cdot C_6H_3(CN) \cdot CH{:}CH \cdot C_6H_4 \cdot OMe$,

yellow needles, m. p. 183°, obtained from the condensation of *o*-nitro-*p*-toluonitrile and salicylaldehyde methyl ether in the presence of a little piperidine at 100°, giving greenish-yellow solutions in benzene and acetic acid, but an orange-coloured one in trichloroacetic acid; this was converted by alcoholic hydrogen chloride into *ethyl 2-nitro-2'-methoxystilbene-4-carboxylate*,

$CO_2Et \cdot C_6H_3(NO_2) \cdot CH{:}CH \cdot C_6H_4 \cdot OMe$,

yellow needles or leaflets, m. p. 101°, the solutions in acetic acid or benzene and trichloroacetic acid showing the same differences in colour as were observed with the parent compound. 2-*Nitro-4-cyano-3'*: *4'-methylenedioxystilbene*,

$NO_2 \cdot C_6H_3(CN) \cdot CH{:}CH \cdot C_6H_3{:}O_2{:}CH_2$,

orange-yellow needles, m. p. 192°, obtained in the same manner as the last nitrile, but using piperonal, which gives yellow solutions in acetone, acetic acid, or benzene, but an orange-coloured solution in trichloroacetic acid. By applying the usual method of condensation to *p*-dimethylaminobenzaldehyde, with *p*-nitro-*o*-toluonitrile and *o*-nitro-*p*-toluonitrile, there were obtained 4-*nitro-2-cyano-4'-dimethylaminostilbene* $NO_2 \cdot C_6H_3(CN) \cdot CH{:}CH \cdot C_6H_4 \cdot NMe_2$, and 2-*nitro-4-cyano-4'-dimethylaminostilbene*, almost black leaflets, with a green lustre, m. p. 209—210°, and lustrous, blackish-green needles, m. p. 178° respectively, the former giving an orange-red solution in benzene with an orange-coloured fluorescence, whilst the latter gives a deep red solution in acetic acid, benzene, or alcohol, and a greenish-yellow solution in trichloroacetic acid. Similarly, by condensation of 2 : 4 : 6-trinitrotoluene with anisaldehyde and *p*-chlorobenzaldehyde respectively there were obtained 2 : 4 : 6-*tri-nitro-4'-methoxystilbene*, $OMe \cdot C_6H_4 \cdot CH{:}CH \cdot C_6H_2(NO_2)_3$, red needles, m. p. 168—169°, and 4'-*chloro-2 : 4 : 6-trinitrostilbene*,

$C_6H_4Cl \cdot CH{:}CH \cdot C_6H_2(NO_2)_3$,

brownish-yellow leaflets, m. p. 154—155°.

Although the two forms of any one of the nitromethoxystilbenes

give identical solutions in any one solvent, the colour of the solution varies considerably with different solvents, ranging from a pale or greenish-yellow in benzene to an orange colour in trichloroacetic acid. This colour variation is regarded, not as a characteristic of the methoxy- or stilbene groups, but as a particular case of the general behaviour of unsaturated organic compounds; thus the corresponding nitromethoxystyrene, as well as the nitromethyl-stilbenes, show a similar effect. It is considered as probable that the differences in colour are due to the formation of compounds between the solvent and solute, somewhat analogous to the "halochromy" of the unsaturated ketones, indeed, 2-nitro-4-cyano-4′-methoxystilbene, which dissolves in sulphuric acid, giving an orange-coloured solution, has its yellow solution in acetic acid turned orange-yellow by the addition of sulphuric acid. The tendency to form such additive compounds as are here postulated is demonstrated by the marked colour change produced by the addition of stannic chloride to the benzene solutions of certain of the above nitromethoxystilbenes, the yellow colour giving way to an orange colour. In certain cases, *additive* compounds of the suggested type were isolated, namely, with 2:4-dinitro-4′-methoxystilbene, $2C_{15}H_{12}O_5N_2,C_6H_6$, orange-red prisms, and $2C_{15}H_{12}O_5N_2,NH_2Ph$, orange-red needles; with 2-nitro-4-benzoylamino-4′-methoxystilbene, *compounds* with 1AcOH, yellow needles, and with $1CCl_3{\cdot}CO_2H$, orange-coloured leaflets, both of which on loss of the additional molecule yield the more deeply orange-coloured modification of the parent substance; similarly, 2-cyano-4-nitro-4′-methoxystilbene gives additive *compounds* with $\frac{1}{2}C_6H_6$, yellow tablets, and with $\frac{1}{2}SnCl_4$, orange-coloured crystals, m. p. near 140°, the former compound regenerating the orange modification, and the latter the yellow modification of the parent substance.

It is suggested that the above phenomena as to two crystalline modifications of one substance and the marked differences in the colour of solutions in various solvents are not due to ordinary isomerism or polymerism, but to influences more physical in nature. The colour changes in solution are referred to the influence of combination with the solvent on the chromophoric character of the nitro-group, whilst the existence of one substance in two modifications of different colour is explained by assuming that in the formation of crystals of the nitromethoxystilbene compounds each nitro-group tends to become attached to a methoxy-radicle in another molecule, so as to form a coloured molecular compound analogous to those produced by the combination of aromatic nitro-compounds with aromatic hydrocarbons or their derivatives, particularly their phenolic ethers. The compounds produced in this way are believed to be those of deep orange colour, the similar colour of solutions in strongly acidic solvents originating in a somewhat analogous manner. In the formation of the yellow crystals of the nitromethoxystilbenes, on the other hand, the molecules are believed to become attached to one another merely by a loose polymerisation, such as is experienced with the butadienes and nitroso-compounds

(compare Pfeiffer, *Zeitsch. anorg. Chem.*, 1915, **92**, 376). The theory can be extended to explain why some of the crystalline additive compounds show similar colour differences to the parent compounds. D. F. T.

Some Applications of the Electronic Conception of Positive and Negative Valencies. VI. The Existence and Properties of Free Radicles. HARRY SHIPLEV FRY (*Zeitsch. physikal. Chem.*, 1915, **90**, 458—480. Compare A., 1911, i, 431; 1912, ii, 713; 1913, ii, 363).—The electron conception of positive and negative valencies developed in previous papers is considered in connexion with free radicles, more particularly the triarylmethyls of Gomberg. It is shown that these substances in many respects are comparable with electro-neutral atoms. Thus the oxidation of triphenylmethyl is shown to be similar to the oxidation of metallic sodium; the addition of iodine or hydrogen by this substance is similar to the addition of these elements by sodium and chlorine respectively. The formation of triphenylmethyl by the action of metallic silver on triphenylmethyl chloride is considered from the electronic point of view, and shown to consist in a reduction of the quadrivalent carbon atom of the triphenylmethyl ion by the silver to a tervalent carbon atom. In addition to the reactions mentioned, the following are also considered from the electronic point of view; the reaction of triphenylmethyl with nitrogen tetroxide; the addition of xylene and acids by triphenylmethyl; the action of light and the electrical conductivity of triphenylmethyl in liquid sulphur dioxide. It is shown that the instability or reactivity and the general chemical properties of the free radicles depend on their developing positive or negative valencies as the result of the loss or gain of negative electrons. This amounts to saying that free radicles may act as oxidising or reducing agents. The power of taking up or expelling electrons is a property of definite atoms in the free radicles, and consequently the valency of these atoms, both with respect to its number and polarity, is variable. Not only are triphenylmethyl and other triarylmethyls to be regarded as free radicles, but also nitrogen tetroxide, sodammonium, tetraethylammonium, and some elements are to be similarly regarded. Intramolecular changes brought about by light in triphenylmethyl are to be explained by means of the electronic formula of benzene. It is shown that the electrical conductivity of triphenylmethyl in sulphur dioxide solution is in many ways analogous to the conductivity of a solution of sodium in liquid ammonia. In the first case the ions are probably $Ph_3C^{\bullet}$ and SO_2', and in the second case $Na^{\bullet}$ and NH_3', and in this case the ions are derived from the existence of the free radicle $NaNH_3$ in solution. The electronic formula of this substance illustrates the mechanism of the formation of sodamide and $Na_2N_2H_6$. J. F. S.

Triphenylmethyl. XXIV. The Additive Compounds of Triphenylmethyl and Some Saturated Hydrocarbons. M. GOMBERG and C. S. SCHOEPFLE (*J. Amer. Chem. Soc.*, 1915, **37**, 2569—2575).—It has already been shown that triphenylmethyl

can form additive compounds with paraffin hydrocarbons, but as the samples then used (Gomberg and Cone, A., 1905, i, 426) may have contained a small amount of olefines, the work has been repeated and extended with carefully purified paraffins, both of natural and synthetic origin.

The method of procedure was to heat triphenylmethyl with the hydrocarbon to the b. p. of the latter and to filter the solution, when, on cooling, triphenylmethyl or an additive compound crystallised out. The nature of the product was examined by cautiously expelling any combined hydrocarbon at 80—110° in a current of carbon dioxide. The results were slightly irregular. The capacity of triphenylmethyl to form additive compounds with paraffin hydrocarbons is definitely proved, but the dissociation temperature of the additive compound is so low in some cases that the above method yields only unaltered triphenylmethyl. Thus with hexane no additive compound was observed, whilst with heptane, also, no additive compound was obtained if crystallisation occurred in the solution whilst still hot, whereas if crystallisation was suspended until the solution had cooled considerably the product consisted mainly of the additive compound $2CPh_3,C_7H_{16}$. With octane, crystallisation always occurred in the hot solution, and only a small percentage of additive compound was present in the product. With decane, it was found possible to obtain a *compound*, $CPh_3,C_{10}H_{22}$, derived from unimolecular triphenylmethyl, which may be explained by the fact that at the b. p. of this liquid triphenylmethyl is mainly in a unimolecular condition. *cyclo*Hexane and methyl*cyclo*hexane, from which triphenylmethyl crystallises at relatively low temperatures, gave *additive* compounds of the general composition $2CPh_3,X$, where X represents the hydrocarbon molecule. D. F. T.

Triphenylmethyl. XXV. Preparation of *p*-Hydroxytriphenylcarbinol and Attempts to Isolate the Corresponding Triarylmethyl. M. GOMBERG and R. L. JICKLING (*J. Amer. Chem. Soc.*, 1915, **37**, 2575—2591).—As *p*-hydroxytriphenylcarbinol is capable of existence in two forms, one coloured and the other colourless (Gomberg and West, A., 1913, i, 72; Gomberg, A., 1913, i, 1056), the question arises as to whether the introduction of a *p*-hydroxy-group into triphenylmethyl causes any tendency to dynamic isomerism in this substance. For this reason the preparation of *p*-hydroxytriphenylmethyl has been attempted.

Diphenylmethylene chloride, CPh_2Cl_2, prepared by the interaction of carbon tetrachloride and benzene in the presence of aluminium chloride (Böeseken, A., 1905, i, 423), reacts with phenol in benzene solution at about 50°, giving diphenoxydiphenylmethane, $CPh_2(OPh)_2$ (compare Mackenzie, T., 1901, **79**, 1209), the product being identical with the substance obtained by Wieland (A., 1911, i, 851). In this preparation it is advisable to aid the removal of hydrogen chloride as fast as it is produced, an effect which is facilitated by the use of the mobile solvent benzene. If the hydrogen chloride is allowed to accumulate, an effect which is assisted by

using phenol and diphenylmethylene chloride without any solvent, there is produced in one to three days a reaction mixture consisting chiefly of *p*-hydroxytriphenylcarbinol; the formation of this substance is to be attributed to intramolecular rearrangement in the diphenoxy-compound, following the stages:

$$CPh_2{<}^{OPh}_{OPh} \longrightarrow CPh_2{<}^{C_6H_4\cdot OH}_{OPh} \xrightarrow{HCl} CPh_2{<}^{C_6H_4\cdot OH}_{Cl} \longrightarrow CPh_2{<}^{C_6H_4\cdot OH.}_{OH}$$

This view of the course of the reaction receives confirmation from the fact that the reaction proceeds more rapidly with a bimolecular proportion of phenol. The *p*-hydroxytriphenylcarbinol is accompanied by a little *pp'*-dihydroxytetraphenylmethane, which is almost the sole product if the reaction is performed at higher temperature, the change then being represented by

$$CPh_2(OPh)_2 \longrightarrow CPh_2(OPh)\cdot C_6H_4\cdot OH \longrightarrow CPh_2(C_6H_4\cdot OH)_2,$$

any *p*-hydroxytriphenylcarbinyl chloride intermediarily produced also being converted by excess of phenol into the same compound.

For the conversion of *p*-hydroxytriphenylcarbinol into the radicle *p*-hydroxytriphenylmethyl, it was first converted into p-*ethylcarbonatotriphenylcarbinol*, needles, m. p. 119°, by the action of ethyl chloroformate; this carbinol, on treatment in benzene solution with hydrogen chloride in the presence of calcium chloride, yielded p-*ethylcarbonatotriphenylcarbinyl chloride*, crystals, m. p. 98°, which, under the action of molecular silver on its benzene solution with exclusion of air, gave a red solution; this solution, when exposed to the air, yielded a small quantity of p-*ethylcarbonatotriphenylmethyl peroxide*, which is strong presumptive evidence of the presence of the free *p*-ethylcarbonatotriphenylmethyl in the red solution. Concentrating the red solution, or boiling, caused the formation of a small quantity of an amorphous, white powder of molecular weight, $C_{44}H_{38}O_6$, which was probably a metameride of the bimolecular form of the free radicle (compare Gomberg, A., 1903, i, 244; Tschitschibabin, A., 1905, i, 125; 1908, i, 624). All attempts to convert *p*-ethylcarbonatotriphenylmethyl peroxide into the corresponding hydroxy-peroxide were unsuccessful, hydrolysis resulting in the formation of *p*-ethylcarbonatotriphenylcarbinol or of *p*-hydroxytriphenylcarbinol. *p*-Ethylcarbonatotriphenylcarbinyl chloride was converted by prolonged agitation in benzene solution with mercuric oxide into *di*-p-*ethylcarbonatotriphenylmethyl ether*, a colourless, crystalline mass, m. p. 219°, which is readily hydrated to the corresponding carbinol.

From *p*-hydroxytriphenylcarbinol there were also obtained by the usual methods *p*-benzoyloxytriphenylcarbinol and *p*-acetoxytriphenylcarbinol, which were converted into the corresponding carbinyl *chlorides*, crystals, m. p. 105°, and needles, m. p. 88°, respectively, the former by the action of hydrogen chloride and calcium chloride on a solution in benzene, the latter by the action of acetyl chloride. By the simultaneous action of molecular silver and oxygen on these chlorides in benzene solution there were obtained

p-*benzoyloxytriphenylmethyl peroxide*, m. p. 167°, and p-*acetoxytriphenylmethyl peroxide*, m. p. 172°. Endeavours to isolate the free radicles from these chlorides yielded, as in the case of *p*-ethylcarbonatotriphenylmethyl chloride, colourless *compounds*, m. p. 266—269° and 255—270° respectively, of the same molecular weight as the bimolecular forms of the unisolated radicles. D. F. T.

Condensation of Acetophenone by Means of Sodium Ethoxide. I. C. GASTALDI and F. CHERCHI (*Gazzetta*, 1915, **45**, ii, 251—275).—The products formed by the condensation occurring when acetophenone is heated in presence of sodium ethoxide at 130—140° include (1) two compounds, m. p. 182° and 145° respectively, to be described later, and (2) 3:5-*diphenyl*-1-*methylbenzene*, $C_6H_3MePh_2$, m. p. 130°, which was formerly described as diphenyl*cyclo*butadiene (A., 1914, i, 514). When oxidised with potassium dichromate and sulphuric acid or with chromic anhydride in acetic acid, this compound yields benzoic acid, whilst with nitric acid (D 1·075) in a sealed tube at 140—150° it gives 3:5-*diphenylbenzoic acid*, $C_6H_3Ph_2\cdot CO_2H$, which crystallises in colourless, prismatic needles, m. p. 260°; the *sodium* ($+4H_2O$) and *potassium* ($+7H_2O$) salts of this acid were prepared. On dry distillation, the sodium salt yields 1:3-diphenylbenzene, m. p. 87°, which forms a tetrabromo-derivative, m. p. 186°; for these two compounds, Olgiati (A., 1895, i, 149) gave m. p. 84—85° and 181° respectively. Oxidation of 3:5-diphenylbenzoic acid by means of potassium dichromate and sulphuric acid yields 1:3:5-benzenetricarboxylic acid.

The products obtained by heating *p*-chloroacetophenone and sodium ethoxide together in an autoclave at 130—140° are: (1) *p*-chlorobenzoic acid; (2) p-*chlorophenylmethylcarbinol*,

$$C_6H_4Cl\cdot CHMe\cdot OH,$$

which is a colourless liquid, b. p. 140—142°/31 mm., and yields a *phenylurethane*, $C_{15}H_{14}O_2NCl$, m. p. 93°; (3) 3:5-*di*-p-*chlorophenylmethylbenzene*, $C_6H_3Me(C_6H_4Cl)_2$, which forms colourless, comma-shaped needles m. p. 175°; (4) 1:3:5-*tri*-p-*chlorophenylbenzene*, $C_6H_3(C_6H_4Cl)_3$, which forms yellow needles, m. p. 235°.

In a similar manner, *p*-tolyl methyl ketone and sodium ethoxide yield: (1) *p*-toluic acid; (2) *p*-tolylmethylcarbinol; (3) 3:5-*di*-p-*tolyltoluene*, $C_6H_3Me(C_6H_4Me)_2$, which forms tufts of prismatic laminæ, m. p. 117°, and has the normal molecular weight in freezing benzene. T. H. P.

Stereochemistry of Quinquevalent Nitrogen. II. Resolution of the Asymmetric Quaternary Ammonium Compounds. SHIGERU KOMATSU (*Mem. Coll. Sci., Kyoto Imp. Univ.*, 1915, **1**, 123—148; *Chem. News*, 1915, **112**, 209, 217, 231, 238, 252, 262. Compare A., 1913, i, 39).—The author has resolved some phenylbenzylmethyl-*n*-propylammonium derivatives and compared the data obtained with those quoted by Wedekind and Fröhlich, with which they agree closely. The platinichloride was found to have m. p. 163·5° and the bromide m. p. 166—167°, $[\alpha]_D^{25}$ −124·3°. He has also resolved the α- and γ-forms of some phenylbenzylmethylallyl-

ammonium derivatives. Comparing the data for the former with those obtained by Pope and Peachey (T., 1899, **75**, 1127) and Pope and Harvey (T., 1901, **79**, 828), it was found that although the m. p.'s did not agree the rotatory powers were closely alike. In the case of the γ-compounds, which have likewise been resolved by the author, the m. p.'s were found to be the same as those obtained by him for the α-derivatives, but the rotatory powers were different. The author's data are: α-*d*-phenylbenzylmethylammonium *d*-camphorsulphonate, m. p. 162—163°, $[\alpha]_D^{25}$ (in water) + 46·7°; γ-*d*-phenylbenzylmethylammonium *d*-camphorsulphonate, m. p. 163°, $[\alpha]_D^{25}$ (in water) + 58·61; α-*l*-phenylbenzylmethylallyl *l*-camphorsulphonate, m. p. 162—163°, $[\alpha]_D^{25}$ (in water) − 46·59°; γ-*l*-phenylbenzylmethylallyl *l*-camphorsulphonate, m. p. 163—164°, $[\alpha]_D^{25}$ (in water) − 56·21°; α-*d*-phenylbenzylmethylallylammonium iodide, m. p. 135—136°, $[\alpha]_D^{25}$ (in chloroform) + 58·28° (? $[\alpha]_D^{25}$ + 54·7°) (in alcohol) $[\alpha]_D^{25}$ + 51·72°; γ-*d*-phenylbenzylmethylallylammonium iodide, m. p. 134—135°, $[\alpha]_D^{25}$ (in chloroform) + 73·98°, (in alcohol) + 65·54° (? $[\alpha]_D^{25}$ + 63·64°); α-*l*-phenylbenzylmethylallylammonium iodide, m. p. 134—135°, $[\alpha]_D^{25}$ (in alcohol) − 51·34°; γ-*l*-phenylbenzylmethylallylammonium iodide, m. p. 135—135·5°, $[\alpha]_D^{25}$ (in alcohol) − 63·15°; α-*d*-phenylbenzylmethylallylammonium bromide, m. p. 155—156°, $[\alpha]_D^{25}$ (in alcohol) + 67·44°; γ-*d*-phenylbenzylmethylallylammonium bromide, m. p. 155—156°, $[\alpha]_D^{25}$ (in alcohol) + 81·80; α-*d*-phenylbenzylmethylallylammonium mercuri-iodide

$$(\alpha\text{-}d\text{-}C_7H_7\cdot NPhMe\cdot C_3H_5I,HgI_2),$$

m. p. 119—120°, $[\alpha]_D^{25}$ (in ethyl acetate) + 24·86°; γ-*d*-phenylbenzylmethylallylammonium mercuric iodide, m. p. 120—121°, $[\alpha]_D^{25}$ (in ethyl acetate) + 39·51°; α-*l*-phenylbenzylmethylallylammonium mercuri-iodide, m. p. 119—120°, $[\alpha]_D^{25}$ (in ethyl acetate) − 24·12°; γ-*l*-phenylbenzylmethylallylammonium mercuri-iodide, m. p. 120°, − 39·60°; α-*d*-phenylbenzylmethylallylammonium platinichloride, m. p. 149—150°; γ-*d*-phenylbenzylmethylallyl platinichloride, m. p. 148—149°. T. S. Pa.

Electrochemical Synthesis of Phenylhydroxylamine. F. M. Frederiksen (*J. physikal Chem.*, 1915, **19**, 696—701).—It is shown that phenylhydroxylamine can be prepared by the electrolytic reduction of nitrobenzene. The best yield (29%) is obtained when a solution of 5 c.c. of nitrobenzene in 250 c.c. of 60% alcohol containing 10 grams of ammonium chloride is electrolysed between zinc electrodes at room temperature. A current of 2 amperes was used, and passed through the solution for 2·67 hours. The product also contains azobenzene. The yields are lower than those obtained by the usual chemical production of these substances. J. F. S.

The Hydrolysis of Sodium Phenoxides in Aqueous Solution. David Runciman Boyd (*T.*, 1915, **107**, 1538—1546).—The degree of hydrolysis of sodium phenoxides in aqueous solution has been determined by measurement of the rate of saponification of methyl acetate at 25°. From the hydrolysis constants (κ_h), the ionisation constants of the phenols are calculated by means of the equation

$\kappa_a = \kappa_w / \kappa_h$, in which $\kappa_w = 1{\cdot}2 \times 10^{-14}$. The numbers obtained vary from $\kappa_a = 1{\cdot}17 \times 10^{-10}$ for guaiacol to $\kappa_a = 0{\cdot}17 \times 10^{-10}$ for mesitol.

The acidity of phenol, as measured by the ionisation constant, is diminished by the introduction of alkyl groups. The effect of substitution is greatest in the ortho-position, slightly less in the para-position, and much less in the meta-position. The *iso*propyl group is more effective than the methyl group in the ortho-position, but there is little difference when the substituents occupy the meta-position. The substitution of a methoxy-group in the ortho-position has scarcely any influence on the acidity of phenol.

It has been observed that mesitol produces an intense red coloration when heated with dilute sodium hydroxide solution.

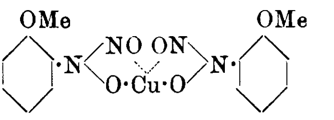
H. M. D.

Esters of Phenols. JOS. A. EINHORN (*Chem. Zentr.*, 1915, ii, 739; from *Bul. Soc. Ştiinte Bucureşti*, 1915, **17**, 51—60).—The following esters were prepared by the action of *iso*valeric acid on the corresponding phenol in presence of phosphoryl chloride: *Phenyl* iso*valerate*, $CHMe_2{\cdot}CH_2{\cdot}CO_2Ph$, a colourless oil of ethereal odour and unpleasant taste, b. p. 225—250°. *Thymol* iso*valerate*, $C_{15}H_{22}O_2$, a colourless liquid, b. p. 248—249°/758 mm., 194°/300 mm., D_{15}^{15} 0·9590. o-*Tolyl* iso*valerate*, $C_{12}H_{16}O_2$, a colourless oil, b. p. 174—178°/700 mm., D_{15}^{15} 0·9894. m-*Tolyl* iso*valerate*, b. p. 185°/750 mm., D_{15}^{15} 0·9895. p-*Tolyl* iso*valerate*, a colourless oil, b. p. 255—257°, D_{15}^{15} 0·9884.

G. F. M.

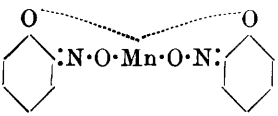
o-**Nitrosophenol. II.** OSKAR BAUDISCH and S. ROTHSCHILD (*Ber.*, 1915, **48**, 1660—1665. Compare A., 1912, i, 441).—Some more metallic compounds of *o*-nitrosophenol are described.

The emerald-green solution of *o*-nitrosophenol in a mixture of light petroleum and ether is a sensitive reagent for copper ions, giving the deep red coloration due to the copper salt. A solution of the reagent is quickly prepared as follows: A mixture of *o*-nitroanisole, amyl nitrite, concentrated aqueous ammonia, and alcohol is vigorously shaken and treated with zinc dust in small portions. After about half an hour, the hot mixture is filtered and the filtrate is mixed with copper acetate and acetic acid. The *copper* salt of *nitroso*-o-*methoxyphenylhydroxylamine* (annexed formula) separates as a silver-grey, crystalline powder, which changes into the copper salt of *o*-nitrosophenol on boiling with xylene, but the yield is poor. On shaking the petroleum solution of this with milk of lime, the intermediate calcium salt is formed, and on acidifying there remains a petroleum solution of the desired *o*-nitrosophenol.



For the preparation of the manganese salt, the ammonium salt of *o*-nitrosohydroxylaminophenyl *p*-toluenesulphonate (which itself forms a pale grey *manganese* salt) is hydrolysed by sodium hydroxide, and the concentrated solution is mixed in the cold with

manganese nitrate and then acidified with metaphosphoric acid. The *manganese* salt of *o*-hydroxynitrosophenylhydroxylamine separates in brown crystals, but it changes spontaneously or on warming into the *manganese* salt of *o*-nitrosophenol (annexed formula). This crystallises from a large volume of alcohol–ethyl acetate as a dark reddish-brown substance. The *aluminium* salt, $C_{18}H_{12}O_6N_3Al$, is almost black. J. C. W.



m-**Nitrosoanisole.** OSKAR BAUDISCH and ROSE FÜRST (*Ber.*, 1915, **48**, 1665—1670).—Following the methods adopted in the preparation of *o*-nitrosophenol from *o*-nitrophenol (A., 1912, i, 441, and preceding abstract), *m*-nitrosoanisole and allied compounds have been isolated.

An alcoholic solution of *m*-nitroanisole was saturated with ammonia and then with hydrogen sulphide, and after a day the ammonium sulphides were completely precipitated by ether. The clear ethereal extract containing the unstable *m*-methoxyphenylhydroxylamine was then dried, saturated with ammonia, and mixed with amyl nitrite, when the *ammonium* salt of *nitroso*-m-*methoxyphenylhydroxylamine*, $OMe{\cdot}C_6H_4{\cdot}N(NO){\cdot}ONH_4$, separated as a remarkably stable, chalk-like powder, m. p. 135°, which is very soluble in water. The aqueous solution gave precipitates of the dark blue *copper* salt, $(C_7H_7O_3N_2)_2Cu$, and yellowish-brown *ferric* salt, $(C_7H_7O_3N_2)_3Fe$, and was oxidised by bromine water at −10° to m-*nitrosoanisole*, $OMe{\cdot}C_6H_4{\cdot}NO$. This is a white, granular substance which melts to an emerald-green liquid at 48° and gives green solutions in organic media. The free *nitroso*-m-*methoxyphenylhydroxylamine*, $OMe{\cdot}C_6H_4{\cdot}N(NO){\cdot}OH$, was liberated from the ammonium salt by means of metaphosphoric acid as a pale yellow, very stable, crystalline powder, m. p. 77°. If, in the oxidation of the ammonium salt, chlorine water or not freshly prepared bromine water is used, the product is a mixture of the free nitroso-*m*-methoxyphenylhydroxylamine and *m*-nitrosoanisole, which can be separated by solution in light petroleum, the former being sparingly soluble in the cold. J. C. W.

m-**5-Xylenol.** K. VON AUWERS and E. BORSCHE. [With A STEINICH.] (*Ber.*, 1915, **48**, 1698—1716).—It has recently been mentioned that when *m*-5-xylenol or its methyl ether is condensed with acetyl chloride by the Friedel-Crafts' reaction, either one or two acetyl groups enter the ortho-positions with regard to the hydroxyl group (A., 1915, i, 145). The constitution of the two ketones is now fully dealt with. Why the para-position should be rejected is inexplicable, for para-derivatives are obtained from *m*-5-xylenol by the most widely differing reactions. The mono-ketone is, moreover, interesting because it contains a carbonyl group between two ortho-substituents. It has been regarded as a rule that such ketones would form no oximes, but although this is true if the substituents are alkyl radicles, it is not so if one happens to be hydroxyl. The

above ketone, and other hydroxy-ketones, are found to react more or less readily with hydroxylamine in the presence of an alkali.

A good yield of 5-methoxy-*m*-xylyl 4-methyl ketone (4-acetyl-*m*-5-xylyl methyl ether) is only obtained by applying the Friedel-Crafts' method at as low a temperature as possible. The ketone (*ibid.*) forms an *oxime*, $OMe{\cdot}C_6H_2Me_2{\cdot}CMe{:}N{\cdot}OH$, brilliant, white prisms, m. p. 135°, and a *semicarbazone*, $C_{12}H_{17}O_2N_3$, m. p. 185°. When the oxime is left with acetic anhydride, it apparently forms an oily acetate, but on boiling it is transformed into 4-*diacetylamino*-5-*methoxy*-m-*xylene*, $OMe{\cdot}C_6H_2Me_2{\cdot}NAc_2$, which crystallises in colourless, flat needles, m. p. 80—81°, and is hydrolysed by boiling alkali hydroxides to the *monoacetyl* compound, stout prisms, m. p. 150·5°. The latter is also obtained by the action of phosphorus pentachloride on the oxime, or even by heating the oxime with hydrochloric acid at 100° in a sealed tube. The oxime therefore suffers the Beckmann transformation very readily, but the acetyl compound is very resistant to hydrolysing agents.

When applying the Friedel-Crafts' synthesis to *m*-5-xylenol itself, it is not so important to keep the mixture cold. The two ketones which are always formed are removed in steam, the diketone remaining until last. The *oxime* of 5-hydroxy-*m*-xylyl 4-methyl ketone (4-acetyl-*m*-5-xylenol), $OH{\cdot}C_6H_2Me_2{\cdot}CMe{:}N{\cdot}OH$, crystallises in glistening, flat needles and prisms, m. p. 143°, and the *semicarbazone*, $C_{11}H_{15}O_2N_3$, forms stout crystals, m. p. 217—218°. When the oxime is boiled with acetic anhydride it forms an oily triacetate, which is hydrolysed by alcoholic alkali hydroxide to 4-*acetylamino*-m-5-*xylenol*, $OH{\cdot}C_6H_2Me_2{\cdot}NHAc$, brilliant scales, m. p. 186—187°. The same acetyl derivative is obtained by saturating an acetic acid solution of the oxime with hydrogen chloride. If the oxime is treated with phosphorus pentachloride, however, the product is the inner anhydro-compound, namely, 2:7:9-*trimethyl*-4:5-*benzoxazole* (*ethenyl*-o-*amino*-m-5-*xylenol*), $C_6H_2Me_2{<}^{N}_{O}{>}CMe$. This base crystallises in flat needles, m. p. 28·5°, b. p. 234—236°, and forms a *hydrochloride*, m. p. 139° (decomp.), a soluble nitrate and sulphate and sparingly soluble platinichloride and *mercurichloride*, glistening needles. When the oxime is boiled with about 20% hydrochloric acid, a little of the anhydride is formed, which can be removed by steam, but the main product is the *hydrochloride* of 4-*amino*-m-5-*xylenol*, $OH{\cdot}C_6H_2Me_2{\cdot}NH_2,HCl$. This crystallises in long, glistening needles, m. p. 270—280°, and yields the free *base*, m. p. 158—159°, when treated with ammonia, or sodium carbonate, acetate, or sulphite. The base reduces silver nitrate, and forms a sodium salt and a *dibenzoate*, $C_{22}H_{19}O_3N$, m. p. 148—149°, which yields 4-*benzoylamino*-m-5-*xylenol*, m. p. 211—212°, when warmed with alcoholic alkali hydroxide.

5-Hydroxy-*m*-xylyl 4:6-dimethyl diketone (4:6-diacetyl-*m*-5-xylenol) (*ibid.*) forms a *dioxime*, $OH{\cdot}C_6HMe_2(CMe{:}N{\cdot}OH)_2$, in thick plates, m. p. 173—174°. It also couples with benzenediazonium chloride to form 4:6-*diacetyl*-2-*benzeneazo*-m-5-*xylenol*, $C_{18}H_{18}O_3N_2$, a ruby-red compound, m. p. 138—139°, which yields an

acetate, orange needles, m. p. 139—140°, and this may be reduced by zinc dust and acetic acid to the *hydrazo*-compound, $C_{20}H_{22}O_4N_2$, silky, white needles, m. p. 175—176°.

When treated with sodium hydroxide and chloroform, the *m*-5-xylenol gives the normal products, the *o*- and *p*-aldehydes, the former of which is volatile in steam. The *2-hydroxy-4 : 6-dimethylbenzaldehyde* crystallises in pleasant smelling needles, m. p. 48—49°, and the para-compound agrees with the 4-hydroxy-2 : 6-dimethylbenzaldehyde obtained by Gattermann by his hydrogen cyanide method (A., 1908, i, 29). The methyl ether of the latter, however, has m. p. 45—47°, and not 18° (*ibid.*, p. 33). *m*-5-Xylenol also behaves normally on nitration, giving *4-nitro-*m*-5-xylenol*, lemon-yellow needles, m. p. 66° (*benzoate*, m. p. 71—72°), and *2-nitro-*m*-5-xylenol*, m. p. 107—108°. By adding acetic acid to a cold solution of the *m*-5-xylenol and sodium nitrite in sodium hydroxide, *2-nitroso-*m*-5-xylenol*, $C_8H_9O_2N$, is obtained in pale brown, glistening prisms, m. p. 182—183°. Finally, the xylenol gives a *2-bromo*-derivative, m. p. 115—116°, when treated with one molecular proportion of bromine diluted with cold acetic acid, a 2 : 4-*dibromo*-compound, m. p. 73—74°, with two molecules of bromine, and the known *s*-tribromoxylenol with three molecules.

J. C. W.

Solidifying and Melting Point of Anethole. ROBERT MELDRUM (*Chem. News*, 1915, **112**, 259—260).—Twenty-two determinations by two methods showed that the solidifying point of anethole varies from 14·5° to 15·7°; the melting point of the substance, as determined by the thermometer bulb method, was found to be 15·8°. Untrustworthy results, due to supercooling, were obtained for the solidifying point when the anethole had been melted at a few degrees above the melting point. When anethole was kept in a stoppered bottle for five months at the ordinary temperature and exposed to light, the solidifying point fell to 5·5°. W. P. S.

The Main Constituent of Japanese Lac. V. Constitution of Hydrourushiol. RIKŌ MAJIMA (*Ber.*, 1915, **48**, 1593—1597.* Compare A., 1914, i, 194, and following abstracts).—It has been shown that hydrourushiol is a *n*-pentadecyl derivative of catechol, but the first assumption that the side-chain is in the meta position with regard to the nearest hydroxyl group is found to be untenable. By contrast with synthetic products of this nature (see also A., 1914, i, 167), by comparison with simpler alkyl derivatives of catechol, and by direct synthesis, it is proved that hydrourushiol is 3-pentadecylcatechol. The isomeric *meta* compounds are designated derivatives of *iso*hydrourushiol. J. C. W.

***iso*Hydrourushiol and its next Lower Homologue.** RIKŌ MAJIMA and IKUYA NAKAMURA (*Ber.*, 1915, **48**, 1597—1603 †).—In order to understand the lack of identity between hydrourushiol dimethyl ether and 1-tetradecyl-(or pentadecyl)-3 : 4-dimethoxybenzenes, these ethers have been prepared by a new process, and

* and *Sci. Rep. Tôhoku Imp. Univ.*, 1915, 4, 271—275. † *Ibid.*, 277—284.

the free alkylcatechols have also been synthesised by the condensation of catechol with the fatty acids in the presence of stannic chloride, which dissolves the higher acids.

Catechol, *n*-pentadecoic acid, and stannic chloride were heated together on the water-bath for two hours, and the product was then diluted with hydrochloric acid and filtered. The residue was washed with water and then with light petroleum, and finally crystallised from xylene, when 3 : 4-*dihydroxy*-1-n-*pentadecoylbenzene* (p-*catechyl tetradecyl ketone*), $C_6H_3(OH)_2\cdot CO\cdot[CH_2]_{13}\cdot CH_3$, was obtained in long, flat crystals, m. p. 100°. This ketone was reduced by means of amalgamated zinc and hydrochloric acid to 3 : 4-*dihydroxy*-1-n-*pentadecylbenzene* (iso*hydrourushiol*),

$$C_6H_3(OH)_2\cdot C_{15}H_{31},$$

which crystallised from xylene in leaflets, m. p. 91°. This differs from hydrourushiol, not only in having a high m. p., but in giving a permanent green colour with alcoholic ferric chloride, the natural isomeride being blackened by this agent.

An alternative to the older preparation of the dimethyl ether of the above (A., 1914, i, 167) involved the condensation of methylvanillin with methyl dodecyl ketone (see below) in the presence of alcoholic sodium hydroxide. The product, 3 : 4-*dimethoxy*-1-γ-*keto*-Δ^{α}-*pentadecenylbenzene*, $C_6H_3(OMe)_2\cdot CH{:}CH\cdot CO\cdot C_{12}H_{25}$, pale yellow, flat prisms, m. p. 67—68°, was reduced by hydrogen and platinum black to the saturated *ketone*, m. p. 62—62·5°, and this by Clemmensen's method to 3 : 4-dimethoxy-1-pentadecylbenzene (*iso*hydrourushiol dimethyl ether). This was demethylated by hydriodic acid at 180—190°, and converted into a *nitro*-derivative, $C_{23}H_{39}O_4N$, pale yellow needles, m. p. 70—71°. Hydrourushiol dimethyl ether differs in forming a dinitro-compound.

Catechol was also condensed with myristic acid, giving 3 : 4-*dihydroxy*-1-n-*tetradecoylbenzene* (p-*catechyl tridecyl ketone*),

$$C_6H_3(OH)_2\cdot CO\cdot C_{13}H_{27},$$

m. p. 103°, and this was reduced to 3 : 4-*dihydroxy*-1-*tetradecylbenzene*, $C_{20}H_{34}O_2$, m. p. 84°. The dimethyl ether of this was prepared, as an alternative to the earlier method, by the condensation of methylvanillin with methyl undecyl ketone to the pale yellow *compound*, $C_6H_3(OMe)_2\cdot CH{:}CH\cdot CO\cdot C_{11}H_{23}$, m. p. 67—67·5°, the reduction of this by catalytic means to 3 : 4-*dimethoxy*-1-γ-*keto-tetradecylbenzene*, $C_{22}H_{36}O_3$, m. p. 54—56°, and the final reduction by amalgamated zinc and hydrochloric acid. This tetradecylveratrole was demethylated and also converted into a *nitro*-compound, m. p. 67—67·5° (compare Johnson and Kohmann, A., 1914, i, 832).

The methyl undecyl and dodecyl ketones required in the above syntheses were prepared by distilling a mixture of barium acetate and barium laurate or tridecoate. As an alternative, some methyl dodecyl ketone was prepared by the acetoacetic ester synthesis. Ethyl sodioacetoacetate was heated with undecyl iodide in a sealed tube, and the *ethyl* α-*acetyltridecoate*, $C_{11}H_{23}\cdot CHAc\cdot CO_2Et$, b. p. 145—150°/1 mm., so formed was hydrolysed. J. C. W.

2 : 3-Dihydroxy-1-*n*-propylbenzene. JUNZO KUROSAWA (*Ber.* 1915, **48**, 1603—1606 *).—In order to compare hydrourushiol with a simple *o*-alkyl derivative of catechol, the propyl compound has been prepared.

o-Eugenol (Claisen and Eisleb, A., 1913, i, 1177) was reduced catalytically to o-*dihydroeugenol*, b. p. 144—146°/25 mm., and this was demethylated by heating with fuming hydrobromic acid in a sealed tube. 2 : 3-*Dihydroxy*-1-n-*propylbenzene* (o-*propylcatechol*), $C_6H_3Pr(OH)_2$, forms colourless needles, m. p. 70—72°, b. p. 150—158°/vac., and behaves like hydrourushiol towards alcoholic ferric chloride, or alkali hydroxide, and in its irritating action on the skin.

o-Eugenol was also converted by means of methyl sulphate into o-*eugenyl methyl ether* (o-*allylveratrole*), b. p. 139—146°/20 mm., and this was reduced to 2 : 3-*dimethoxy*-1-n-*propylbenzene* (o-*propylveratrole*), $C_6H_3Pr(OMe)_2$, b. p. 134—137°/22 mm. Like hydrourushiol dimethyl ether, this forms a *nitro*-derivative, b. p. 185—186°/20 mm., and a *dinitro*-compound, $C_{11}H_{14}O_6N_2$, pale yellow, long, monoclinic tablets, m. p. 91—91·5°.

For comparison, 3 : 4-dihydroxy-1-*n*-propylbenzene and its dimethyl ether (*p*-propylveratrole) were prepared from eugenol. They behave like *iso*hydrourushiol and its dimethyl ether. J. C. W.

The Main Constituents of Japanese Lac. VI. Synthesis of Hydrourushiol. RIKŌ MAJIMA and JOSHIHIDE TAHARA (*Ber.* 1915, **48**, 1606—1611 †).—Many of the more obvious methods were tried without success before the authors achieved the synthesis of hydrourushiol dimethyl ether by the condensation of 2 : 3-dimethoxyphenylpropionyl chloride with the sodium compound of α-dodecinene, followed by reduction of the acetylenic ketone.

Methyl laurate was reduced to dodecan-α-ol, and the palmitate of this was converted by dry distillation into dodecylene, the dibromide of which was boiled with alcoholic potassium hydroxide. The dodecinene so obtained was purified through the silver compound. The acetylene was added to granulated sodium suspended in ether in a tube, which was evacuated and sealed, and then warmed at 60° for an hour, when a white, crystalline mass of the sodium compound was formed. The cold tube was then opened in an atmosphere of nitrogen, and β-2 : 3-dimethoxyphenylpropionyl chloride (prepared by the action of thionyl chloride on the acid; Perkin and Robinson, T., 1914, **105**, 2387) was introduced. The tube was again sealed and shaken at 60° for two hours. After extracting the product with ether and water and removing any acids by means of sodium hydroxide, an oil was obtained, which was forthwith reduced by catalytic means to β-2 : 3-*dimethoxyphenylethyl dodecyl ketone*, $C_6H_3(OMe)_2{\cdot}C_2H_4{\cdot}CO{\cdot}C_{12}H_{25}$. This crystallised in flat needles, m. p. 47—49°, and was reduced by Clemmensen's method to 2 : 3-*dimethoxy*-1-n-*pentadecylbenzene* (hydrourushiol dimethyl ether), m. p. 36—37°.

Some new compounds were encountered during the abortive

* and *Sci. Rep. Tôhoku Imp. Univ.*, 1915, 4, 285—288. † *Ibid.*, 289—295.

attempts to synthesise hydrourushiol. Thus, *o*-eugenol was converted into the *acetate*, b. p. 146—148°/15 mm., by means of cold acetic anhydride and sulphuric acid, and this was oxidised by ozone. The product contained *2-acetoxy-3-methoxyphenylacetic acid*, $OMe\cdot C_6H_3(OAc)\cdot CH_2\cdot CO_2H$, m. p. 146°, and the corresponding aldehyde, which was identified as the *semicarbazone*, $C_{12}H_{15}O_4N_3$, m. p. 179·5°. Before attempting the successful synthesis with dodecinene, the less costly sodium compound of hexadecinene was condensed with 2:3-dimethoxyphenylpropionyl chloride, and the product was reduced to *β-2:3-dimethoxyphenylethyl hexadecyl ketone*, $C_6H_3(OMe)_2\cdot C_2H_4\cdot CO\cdot C_{16}H_{33}$, m. p. 57°. J. C. W.

Spirans. VII. Ring Formation with Spirans. HERMANN LEUCHS and LUDWIG LOCK (*Ber.*, 1915, **48**, 1432—1443).—Attention has already been drawn to the special case of asymmetry caused by a spiran carbon atom (Leuchs and Gieseler, A., 1912, i, 714; Leuchs and Lemcke, A., 1915, i, 378), and in an attempt to extend the experimental work in this field the ketonic groups in the molecular-asymmetric bishydrindone-ββ-spiran have been submitted to reduction and to the action of organo-magnesium compounds.

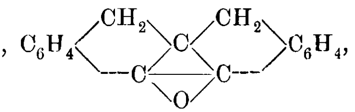
Bishydrindone-ββ-spiran (1 mol.) reacts with magnesium benzyl chloride (2 mols.), giving *bis-1-hydroxy-1-benzylhydrindene-2:2-spiran*, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{C(CH_2Ph)(OH)}>C<\genfrac{}{}{0pt}{}{CH_2}{C(CH_2Ph)(OH)}>C_6H_4$, prisms, m. p. 167—169°, together with smaller quantities of *1-hydroxy-1-benzylhydrindenehydrindone-2:2-spiran*,

$$C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{C(CH_2Ph)(OH)}>C<\genfrac{}{}{0pt}{}{CH_2}{CO}>C_6H_4,$$

hexagonal leaflets, m. p. 180—182°, in which one ketonic group has remained unaffected, and the simple anhydride of the normal dihydroxy-product, *bis-1-benzylhydrindene-2:2-spiran-1:1′-oxide*, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2\text{——}}{C(CH_2Ph)\text{—O—}}>C<\genfrac{}{}{0pt}{}{\text{——}CH_2}{C(CH_2Ph)}>C_6H_4$, m. p. 88°, which can also be obtained from its parent compound by boiling with acetyl chloride.

In a similar manner, the analogous reaction with magnesium phenyl bromide yields *bis-1-hydroxy-1-phenylhydrindene-2:2-spiran*, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{CPh(OH)}>C<\genfrac{}{}{0pt}{}{CH_2}{CPh(OH)}>C_6H_4$, prisms, with $3H_2O$, from moist alcohol, m. p. 125—130°, with subsequent re-solidification and re-fusion at 162—164°, needles from benzene, m. p. 143° (decomp.); this was accompanied by a little *bis-1-phenylhydrindene-2:2-spiran-1:1′-oxide*, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{CPh\text{—O—}}>C<\genfrac{}{}{0pt}{}{CH_2}{CPh}>C_6H_4$, hexagonal tablets, m. p. 95°, which can be obtained more conveniently by boiling the ditertiary alcohol with acetyl chloride.

Difficulties were encountered in the reduction of the diketone, but zinc amalgam with hydrochloric acid gave the most satisfactory result, the products being *1:1′-dehydrobishydrindene-2:2-spiran-*

1:1'-*oxide*,  needles, m. p. 197—201° or 210—211° if in a vacuum. There were also formed at the same time *bishydrindene*-2:2-*spiran*, $C_6H_4<{CH_2 \atop CH_2}>C<{CH_2 \atop CH_2}>C_6H_4$, prisms, m. p. 63°, which can be distilled undecomposed under a pressure of 15 mm., and a *hydrocarbon*, $C_{17}H_{12}$, leaflets, m. p. 210°. The latter compound was also obtained in small quantity when bishydrindone-2:2-spiran was heated with hydriodic acid and red phosphorus at 125—130°, the main product in this case being a *hydrocarbon*, $C_6H_4<{CH_2\cdot CH\cdot C_6H_4 \atop CH_2\cdot CH\cdot CH_2}$ (needles or prisms, m. p. 66—67°, which can be distilled undecomposed under a pressure of 15 mm.), a little 2-o-*carboxybenzylhydrindene*, $C_{17}H_{16}O_2$, needles, m. p. 158—159°, being also formed.

The ditertiary alcohols obtained by the Grignard reaction appeared to be homogeneous, steric influences probably accounting for this unexpected result. It is believed that these products are racemic compounds, in which the configuration is such that the hydroxyl groups are in juxtaposition; they are therefore designated *syn*-compounds, in order to distinguish them from the possible stereoisomeric racemates. D. F. T.

Mercury Double Salts of Aromatic Tellurides. KARL LEDERER (*Ber.*, 1915, **48**, 1422—1425).—A description of double salts (compare Lederer, A., 1914, i, 275) prepared by shaking an ethereal solution of an aromatic telluride with an aqueous solution of mercuric bromide, or by mixing alcoholic solutions of a telluride and mercuric iodide.

Diphenyl telluride mercuribromide, $C_{12}H_{10}Te,HgBr_2$, forms very pale yellow needles, m. p. 148°, with sintering at 143°; the *mercuri-iodide*, $C_{12}H_{10}Te,HgI_2$, golden-yellow needles, m. p. 146°, with sintering at 140°.

Di-o-tolyl telluride mercuribromide, $C_{14}H_{14}Te,HgBr_2$, forms needles or elongated plates, m. p. 199—200°, with sintering at 195°; the *mercuri-iodide*, $C_{14}H_{14}Te,HgI_2$, sulphur-yellow scales, m. p. 142—143°.

Di-p-tolyl telluride mercuribromide, $C_{14}H_{14}Te,HgBr_2$, is a yellow, resinous, amorphous solid, m. p. 64—85°; the *mercuri-iodide*, $C_{14}H_{14}Te,HgI_2$, is a sulphur-yellow, amorphous, resinous solid, m. p. 50—65°.

Di-p-*anisyl telluride mercurichloride*, $C_{14}H_{14}O_2Te,HgCl_2$, is a brown, amorphous substance of no m. p.; the *mercuribromide*, $C_{14}H_{14}O_2Te,HgBr_2$, forms a brown, amorphous substance of no m. p.

If an aqueous solution of basic mercuric nitrate is shaken with an ethereal solution of di-*o*-tolyl telluride, a *compound*,

$$C_{14}H_{15}TeHgNO_4,$$

is obtained as a white precipitate. D. F. T.

The Valency Problem of Sulphur. II. Mercury Thiophenol. [Phenylmercaptide.] H LECHER (*Ber.*, 1915, **48**, 1425—1432).—The author has recently suggested (A., 1915, i, 532) that the variation of the colour of certain aromatic disulphides with change in temperature is due to a loosening of the S-S valency. In confirmation of this explanation an examination has been made of mercury phenylmercaptide, which is known to dissociate into mercury and diphenyl disulphide at higher temperatures. If the change in the colour of diphenyl disulphide is due to a loosening of the central valency of the molecule, mercury phenylmercaptide should likewise show a deepening in colour, because dissociation will be naturally preceded by a weakening of the bond attaching the SPh group to the mercury atom. The expected colour change is found actually to occur in the case of mercury phenylmercaptide and also of mercury *p*-dimethylaminophenylmercaptide.

Mercury phenylmercaptide was prepared by shaking together yellow mercuric oxide and a pyridine solution of phenylmercaptan; the product consists of colourless needles, m. p. 152·5—153·5° (partial decomp.), which gradually became yellow as the temperature rises; it is very soluble in pyridine, and the solution also shows the development of the yellow colour when the temperature is raised. The small electrical conductivity of the solution gives no support for the possibility of the presence of an additive compound behaving as an ionised complex salt.

When mercury phenylmercaptide is distilled under reduced pressure, it decomposes quantitatively into mercury and phenyl disulphide. In indifferent solvents, such as benzene and xylene at 140° and higher, a similar dissociation also occurs, but the reaction is not complete in this case, a state of equilibrium being attained.

D. F. T.

Catalytic Reduction. X. Reduction of Aromatic Alcohols, Aldehydes, and Ketones. A. SKITA [with W. BRUNNER] (*Ber.*, 1915, **48**, 1685—1698).—It has been shown that although aromatic substances can seldom be reduced to hydrocyclic compounds except in glacial acetic acid solution, the reduction of ketones and aldehydes to alcohols can frequently be realised in other media, especially if more platinum is used (compare this vol., i, 16). The question therefore arose, in what order does the complete reduction of an aromatic aldehyde or ketone proceed, and can such substances, by altering the conditions or protecting the carbonyl group, be reduced to the corresponding hydrocyclic compounds?

Experiments with benzaldehyde and benzophenone threw little light on this question, for these were reduced in acetic acid solution directly to the hydrocarbons and the corresponding hydrocyclic hydrocarbons. In the case of cinnamaldehyde, however, the course of the reduction is plainer, for the compounds representing the separate stages can be isolated. First, the ethylene linking disappears, then the aldehyde is reduced to the alcohol, then the benzene nucleus is reduced, and the chief product of the reduction becomes *cyclo*hexylpropyl alcohol. The formation of a small

amount of propylbenzene and propyl*cyclo*hexane indicates that the reduction does also proceed to a slight extent as in the case of benzaldehyde. Phenylacetaldehyde also gives *cyclo*hexylethyl alcohol as the chief product, but the hydrocarbons are formed to a greater extent. In this case, the protection afforded by masking the aldehyde group is illustrated, for the alcohol is more easily obtained by reduction of the acetate, $C_6H_5 \cdot CH \colon CH \cdot OAc$. Acylation is not a general means of protection, however. Benzyl acetate, benzyl benzoate, and benzylidene diacetate are reduced, like benzyl alcohol and benzaldehyde, to toluene. The hydrolysis which accompanies the reduction is so powerful that even benzyl ethyl ether yields toluene. In order to protect the carbonyl groups in benzaldehyde and benzophenone, the condensation with aniline is found to be effective.

Very frequently it has been noticed that reductions proceed more rapidly in the presence of chloroplatinic acid than with pure colloidal platinum, and it seems, therefore, that the unsaturated compound must unite with the platinum compound as a precursor to the action of the hydrogen. Such double compounds would only be formed if the concentration of platinum were sufficiently great or if the union were promoted by some other substance, acetic acid being a notable example.

Reduction of Cinnamaldehyde.—When reduced in the presence of palladous chloride and gum arabic in aqueous-alcoholic solution the product was chiefly β-phenylpropaldehyde, b. p. 224°, mixed with a little cinnamyl alcohol. In acetic acid solution, in the presence of platinic chloride, gum arabic, and a trace of colloidal platinum, it yielded, under one set of conditions, γ-phenylpropyl alcohol, b. p. 235° [acetate, b. p. 243—244° (corr.)], with a trace of propylbenzene, and under other conditions, using more platinic chloride, γ-cyclo*hexylpropyl alcohol*, $C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$, a clear liquid with penetrating odour, b. p. 222—224°, D^{20} 0·9358. The pure alcohol was obtained by hydrolysing the *acetate*, $C_{11}H_{20}O_2$, b. p. 120—121°/15 mm., D^{20} 0·9398, and was oxidised to β-cyclo*hexylpropaldehyde*, $C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot CHO$, a liquid with a powerful aldehydic odour, b. p. 87—88°/15 mm., which was purified by the hydrolysis of the *semicarbazone*, $C_{10}H_{19}ON_3$, m. p. 128° (corr.), with oxalic acid.

Reduction of Phenylethyl Acetate.—This, the first reduction product of the acetate of phenylvinyl alcohol, the enol form of phenylacetaldehyde, was reduced by the same means, and the product was removed in a current of steam after rendering the mixture alkaline. In this way, β-cyclo*hexylethyl alcohol*,

$$C_6H_{11} \cdot CH_2 \cdot CH_2 \cdot OH,$$

was obtained as a liquid with the odour of rose oil, b. p. 206—209°, which formed an *acetate*, b. p. 104°/15 mm., and was oxidised by chromic acid to cyclo*hexylacetaldehyde*, $C_6H_{11} \cdot CH_2 \cdot CHO$, b. p. 79—80°/10 mm. (*semicarbazone*, $C_9H_{17}ON_3$, m. p. 153°).

Reduction of Benzaldehyde to Hexahydrobenzaldehyde.—Benzaldehyde was condensed with aniline, and the benzylideneaniline was reduced by sodium and alcohol to benzylaniline. This was

treated in the above manner, and the product of the reduction was rendered alkaline and distilled in steam, when *dodecahydrobenzylaniline* [cyclo*hexyl*cyclo*hexylmethylamine*], $C_6H_{11}\cdot CH_2\cdot NH\cdot C_6H_{11}$, was obtained as an oil, b. p. 270°, *hydrochloride*, m. p. 305° (corr.), mixed with *cyclo*hexylamine and methyl*cyclo*hexane. The base was oxidised and hydrolysed by permanganate in aqueous-acetone solution to hexahydrobenzaldehyde, $C_6H_{11}\cdot CHO$, b. p. 160—165° [semicarbazone, m. p. 167° (corr.), identical with that obtained by Wallach].

Reduction of Benzophenone to Hexahydrobenzophenone.—Benzophenone was condensed with aniline, the diphenylmethyleneaniline was reduced by sodium and alcohol to benzylhydrylphenylamine (b. p. 224—225°/12 mm.), and this was treated as above. The products obtained were *cyclo*hexylamine, b. p. 134°, and *di*cyclo*hexylmethane*, $CH_2(C_6H_{11})_2$, b. p. 247—248°, but chiefly cyclo*hexylamino*cyclo*hexylphenylmethane*, $C_6H_{11}\cdot CHPh\cdot NH\cdot C_6H_{11}$, b. p. 189°/12 mm., *hydrochloride*, m. p. 276—277° (corr.). The base was oxidised and hydrolysed by chromic acid to *cyclo*hexyl phenyl ketone, $C_6H_{11}\cdot COPh$, which was characterised by the oxime, m. p. 111° (V. Meyer, 1897), and *semicarbazone*, m. p. 175°.

J. C. W.

Some Colour Reactions of Triphenylmethane Derivatives.

E. Noelting and A. Kempf (*Bull. Soc. chim.*, 1915, [iv], **17**, 385—389. Compare Baeyer and Villiger, A., 1902, i, 769; 1903, i, 811; 1904, i, 308, 786, 898).—For the most part a summary of work already published on this subject. The authors have prepared *phenyl-di*-6-*methoxy*-m-*tolylcarbinol* and *phenyl-di*-4-*methoxy*-o-*tolylcarbinol* by oxidation of the corresponding leuco-derivatives prepared by Feuerstein and Lipp (compare A., 1902, i, 768), and have shown that the first carbinol dissolves in sulphuric acid, giving a red coloration, and dyes cotton mordanted with tannin a deep red, whilst the second carbinol dissolves in sulphuric acid, giving a Bordeaux-red colour, but does not dye cotton.

Rosolic acid, which does not dye mordanted cotton, dyes it if the cotton is first treated with tannin. The same applies to the hexamethoxy-derivative of rosolic acid and to trianisylcarbinol. Phenyldianisylcarbinol behaves in much the same way as trianisylcarbinol, but dyes the cotton a much redder orange.

The authors disagree with the view of Baeyer and Villiger that the coloration of methane derivatives with sulphuric acid is due to formation of the corresponding carbinol by oxidation, since the original methane derivative is precipitated unchanged on pouring the solution into water, and, further, if this dilute acid solution is nearly neutralised, it does not dye cotton treated with tannin.

The introduction of simple or substituted amino-groups into triphenylmethane does not modify its reaction with sulphuric acid. In the case of leuco-bases containing a simple or substituted amino-group, the introduction of more than one hydroxyl group into the same benzene nucleus results in a coloration being obtained with

sulphuric acid, the colour deepening as the number of hydroxyl groups increases. W. G.

The Displacement of Halogen in Optically Active Phenylhalogenoacetic Acids by the Anilino-group. ALEX. MCKENZIE and STANLEY CHARLES BATE (T., 1915, **107**, 1681—1685).—When heated with aniline in the presence of water and sodium hydroxide, *l*-phenylchloroacetic acid gave an anilino-acid having $[\alpha]_D +25°$ in acetone. In similar circumstances, *d*-phenylchloroacetic acid gave a lævorotatory anilino-acid. *l*-Phenylchloroacetic acid heated with aniline in presence of dry benzene gave an anilino-acid having $[\alpha]_D +72°$ in acetone, whilst the same acid when boiled with aniline for a short time gave an anilino-acid having a very slight dextro-rotation. There is thus a great difference in the extent to which racemisation takes place in these three cases. Less racemisation occurred when *l*-phenylbromoacetic acid was used instead of the chloro-acid. *r*-Phenylanilinoacetic acid was resolved by means of cinchonine; *l*-phenylanilinoacetic acid has m. p. 188°, and $[\alpha]_D$ $-117{\cdot}9°$, $[\alpha]_{5461}$ $-143{\cdot}5°$ in acetone, $c=1{\cdot}467$. T. S. PA.

Experiments on the Walden Inversion. X. Displacement Reactions with *l*-Phenylbromoacetic Acid. ALEX. MCKENZIE and NELLIE WALKER (T., 1915, **107**, 1685—1701. Compare *T.*, 1913, **103**, 687).—The authors have undertaken a study of the Walden inversion with *l*-phenylbromoacetic acid in order to compare the results with those obtained with *l*-phenylchloroacetic acid, especially in regard to hydroxylation by means of water. *r*-Phenylbromoacetic acid was resolved by means of morphine. The less soluble salt is morphine *l*-phenylbromoacetate, and the bromoacetic acid, m. p. 87—88°, separated from this had $[\alpha]_D^{13\cdot5}$ $-147°$, $[\alpha]_{5461}$ $-178{\cdot}2°$ ($c=2{\cdot}0065$ in benzene). When *l*-phenylbromoacetic acid is acted on by silver carbonate, silver nitrate, silver oxide, mercurous nitrate, mercuric nitrate, mercuric oxide, lead monoxide, lead hydroxide, lead nitrate in the presence of water, dextrorotatory mandelic acid, varying largely, however, in rotation is obtained. With copper sulphate the mandelic acid formed has no rotation. When *l*-phenylbromoacetic acid in aqueous solution is kept for some time, the mandelic acid ultimately isolated is slightly dextrorotatory, this behaviour being different from that which had been observed by McKenzie and Clough (T., 1908, **93**, 811; 1909, **95**, 777] in the case of *l*-phenylchloroacetic acid. The amount of racemisation, however, is very great, and it is found by observing on the one hand the rate of change of rotation of the aqueous solution, and on the other the rate of increase of acidity of the solution, that the rate of racemisation is greater than the rate of displacement of the bromine by hydroxyl, this being particularly the case when the acid is dissolved in a mixture of acetone and water in equal proportions. *l*-Phenylbromoacetic acid when acted on by ammonia yields a phenylaminoacetic acid of a high dextro-rotation, but when the acid, dissolved in dry benzene, is acted on by ammonia, a lævorotatory phenylamino-

acetic acid is obtained. Since, in the experiments described, *l*-phenylbromoacetic acid may be converted by the action of water into a mixture of *r*- and *d*-mandelic acids, but also, under other conditions, into a mixture of *r*- and *l*-mandelic acids, a Walden inversion must take place in one case and not in the other, as shown in the following scheme:

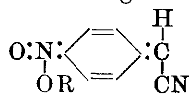
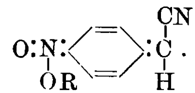
$$\begin{tikzcd} l\text{-}CHPhBr\cdot CO_2H \arrow[r, shift left, "H_2O"] \arrow[d, "H_2O"] & d\text{-}OH\cdot CHPh\cdot CO_2H \arrow[l, shift left, "PBr_5"] \\ l\text{-}OH\cdot CHPh\cdot CO_2H \arrow[r, shift left, "PBr_5"] & d\text{-}CHPhBr\cdot CO_2H \arrow[l, shift left, "H_2O"] \arrow[u, "H_2O"'] \end{tikzcd}$$

The formation of dextrorotatory mandelic acid from *l*-phenylbromoacetic acid is regarded as being due to the following three changes: I. l-$CHPhBr\cdot CO_2H + H_2O = HBr + r$- and l-$OH\cdot CHPh\cdot CO_2H$. The reversible reaction of hydrobromic acid on mandelic acid then proceeds slowly, the slight excess of *l*-hydroxy-acid being converted into *d*-phenylbromoacetic acid, with accompanying racemisation, thus: II. r- and l-$OH\cdot CHPh\cdot CO_2H + HBr = H_2O + r$- and d-$CHPhBr\cdot CO_2H$; the *d*-bromo-acid is then quickly transformed into a mixture of *r*- and *d*-hydroxy-acids: III. r- and d-$CHPhBr\cdot CO_2H + H_2O = HBr + r$- and d-$OH\cdot CHPh\cdot CO_2H$. This assumes that a lævorotatory mandelic acid could be isolated if the reaction were stopped when reaction II had not proceeded far, but that, given sufficient time, a dextrorotatory mandelic acid could be extracted from the solution. This appears to involve a different mechanism for reactions I and II. T. S. PA.

Chromo-isomeric Salts and Chromo-esters of *p*-Nitrobenzyl Cyanide (*p*-Nitrophenylacetonitrile). I. LIFSCHITZ and F. W. JENNER (*Ber.*, 1915, **48**, 1730—1740).—An explanation of the formation of different coloured salts of aromatic nitro-compounds is rather difficult in the case of a complicated substance like *p*-nitrophenylnitromethane. As Hantzsch has shown (A., 1907, i, 500), this compound forms four differently coloured salts, but in spite of the criteria recently established by him (A., 1915, i, 550) it is impossible to determine directly the nature of the isomerism existing between them. It seemed, therefore, to be advisable to search for a simpler compound which would give more well-defined and stable salts, and possibly the corresponding esters. *p*-Nitrophenylacetonitrile satisfies some of these requirements. It forms two isomeric sodium salts, one of which gives a red alcoholic solution and is the more stable towards alkalis, whilst the other gives a green solution and is obtained by leaving the red solution for some time or treating it with carbon dioxide. These are therefore analogous to the green and violet salts of *p*-nitrophenylnitromethane. Since they are the only salts which can be prepared from the nitrile, the yellow and red salts of *p*-nitrophenylnitromethane are due to the participation of the nitro-group attached to the aliphatic chain.

The green salt gives rise to green esters, which are the first really stable esters of aromatic nitro-compounds. The spectra of

the red and green compounds are identical in the ultraviolet and analogous in the visible region, and, therefore, the green salt, like the red (Hewitt, Pope, and Willett, T., 1912, **101**, 1770) and the green ester, must have a quinonoid configuration. To explain the different colour by involving the residual affinities of the nitro- and cyano-groups in a 7- or 8-ring would seem rather strained, and the authors therefore regard the salts as stereo-isomerides, thus:


and


p-Nitrophenylacetonitrile was dissolved in just sufficient boiling alcohol, mixed with the required amount of sodium or potassium ethoxide or rubidium hydroxide, quickly cooled, and poured into ether. The *sodium*, *potassium*, and *rubidium* salts were obtained as almost black powders, which dissolved in alcohol with permanganate colour. They gradually changed in the solid state, especially at above 100°, more quickly in solution, into the green *isomerides*. The latter gave green solutions in alcohol, which changed to permanganate-red on adding an alkaline ethoxide, only to be restored to green on treating with a cyanide or carbon dioxide.

The green alkali salts were converted into the impure green silver salt, which was shaken with methyl iodide and acetone, when it yielded the dark green *dimethyl ester*,

$$OMe{\cdot}ON{:}C_6H_4{:}C{:}C{:}NMe.$$

This crystallised with 1 mol. of acetone, and had an odour of carbylamine. The green alcoholic solution became dark blue on adding potassium hydroxide, and on boiling the ester with alkalis or hydrochloric acid, dark coloured, complicated products were obtained. The *monomethyl ester*, $OMe{\cdot}ON{:}C_6H_4{:}CH{\cdot}CN$, was prepared by boiling the green sodium salt with methyl iodide and methyl alcohol, evaporating almost to dryness, and then quickly stirring the mass into water at 40°, so as to dissolve the sodium iodide. The crude ester melted, was immediately frozen again, filtered off, and crystallised from ether, when it was obtained in glistening, green aggregates, m. p. below 40°. The green, alcoholic solution gave the permanganate-red solution of the metallic salt on adding an alkali hydroxide, or the pale solution of *p*-nitrophenylacetonitrile on treatment with hydrochloric acid. The ester could be kept in a vacuum for about two days, but it changed spontaneously into 4-nitro-3-methylphenylacetonitrile,

$$NO_2{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}CN.$$

This was crystallised alternately from alcohol and water, and found to have m. p. 63° (compare Barger and Ewins, T., 1910, **97**, 2253), and it was oxidised by alkaline permanganate to 6-nitro-*m*-toluic acid, m. p. 220°. J. C. W.

An Antipyretic, *o*-Sulphonylaminobenzo-*p*-phenetidide, and Process for Producing the Same. J. LAGUTT (*U.S. Pat.*, 1153121, 1915; from *J. Soc. Chem. Ind.*, 1915, **34**, 1072).—*o*-Benzoylsulphimide heated with *p*-phenetidine in molecular proportions gives

o-sulphonylaminobenzo-*p*-phenetidide, which forms white, tasteless, lustrous crystals, m. p. 171—172°, soluble in water and alcohol.

G. F. M.

Esters of Polycinnamic Acid. C. LIEBERMANN, G. MÜHLE, and M. KARDOS (*Ber.*, 1915, **48**, 1645—1648. Compare A., 1913, i, 476). —When allyl cinnamate is exposed to light, it changes to a polymeride, which is freely soluble in chloroform, quite insoluble in methyl alcohol, and cannot be saponified. If this flocculent powder is kept at about 140° it becomes insoluble in chloroform, but the new polymeride is still not saponifiable. These "light polymerides" therefore differ from the "heat polymerides" (*loc. cit.*) in respect to hydrolysis, but there is the same analogy between the two pairs, namely, that the polymeride which is soluble in chloroform becomes insoluble on heating.

The "light polymeride" of ethyl cinnamate which was supposed to be sparingly soluble (A., 1911, i, 370) is now shown to contain about 5% of a polymeride which is freely soluble in chloroform, both being indifferent towards alcoholic potassium hydroxide. The "light polymeride" of methyl cinnamate, however, is very soluble in chloroform, but changes to an insoluble form on heating at 140°, whereas the polymeric benzyl and octyl esters do not diminish in solubility in cold chloroform when heated for a long time. J. C. W.

New Method for the Preparation of *allo*Chrysoketonecarboxylic Acid and its Derivatives. Intramolecular Friedel-Crafts' Reaction with Acid Anhydrides. ALFRED SCHAARSCHMIDT (*Ber.*, 1915, **48**, 1826—1833).—Whereas the 2-benzoylanthraquinones on reduction yield anthranol derivatives, the 1-substituted isomerides give intensely blue coloured products (Schaarschmidt, A., 1915, i, 566, 696). In order to elucidate the course of reaction in the latter case, the author has attempted the production of 1-benzoylfluorenone with the idea of examining the behaviour of this on reduction.

For this purpose, 1-phenylnaphthalene-2:3-dicarboxylic acid anhydride was obtained by heating phenylpropiolic acid with acetic anhydride. In an endeavour to prepare fresh derivatives, this compound was heated at 70° in suspension in benzene together with aluminium chloride, with the hope of effecting a condensation with the benzene, but unexpectedly it was found that the product was *allo*chrysoketonecarboxylic acid (Bucher, A., 1908, i, 791; Stobbe, A., 1907, i, 765), which it had been intended to prepare by one of the known methods. The chemical change had therefore been one of internal condensation according to the representation

$$C_6H_5\cdot C_{10}H_5<\begin{matrix}CO\\CO\end{matrix}>O \longrightarrow \begin{matrix}CO-\\ | \\ C_6H_4\end{matrix}>C_{10}H_5\cdot CO_2H.$$

[With N. IRINEU.]—Phosphorus pentachloride converts a suspension of *allo*chrysoketonecarboxylic acid in boiling toluene into the corresponding *chloride*, $C_{18}H_9O_2Cl$, golden-yellow needles, m. p. 194—195°, which on treatment in suspension in chlorobenzene with aluminium chloride yields 1-p-*chlorobenzoyl*allo*chrysoketone*,

$\begin{matrix} CO-- \\ | \\ C_6H_4 \end{matrix}\!\!>C_{10}H_5\cdot CO\cdot C_6H_4Cl$, golden-yellow needles, m. p. 220°; this substance dissolves in sulphuric acid, giving a brownish-red colour, which is not affected by the addition of copper powder (compare Schaarschmidt, *loc. cit.*). In a similar manner by the Friedel-Crafts reaction, applying *m*-xylene as the second reagent, 1-*dimethylbenzoyl*allo*chrysoketone*, $\begin{matrix} CO-- \\ | \\ C_6H_4 \end{matrix}\!\!>C_{10}H_5\cdot CO\cdot C_6H_3Me_2$, orange-yellow platelets, m. p. 212°, can be obtained. The fact that this substance and the preceding one give no striking colour reaction with sulphuric acid and copper powder is not regarded as definite disproof of the power of the 1-benzoylfluorenones to form coloured reduction products; *allo*chrysoketonecarboxylic acid readily undergoes reduction with ammonia and zinc dust, giving the corresponding *alcohol*, $C_{18}H_{12}O_3$, needles, m. p. 244—246° (decomp.), and this reducibility of the carbonyl group in the above compounds may interfere with a course of reduction analogous to that observed with the 1-benzoylanthraquinones.

Ethyl *allo*chrysoketonecarboxylate forms needles, m. p. 182—183°, the colour of which is orange, instead of yellow as stated by Stobbe (*loc. cit.*); the *methyl* ester forms orange needles, m. p. 146—147°; the freshly prepared silver salt is pure yellow.

D. F. T.

Nitrated Proteins. IV. The Identification of 3-Nitrotyrosine among the Products of Hydrolysis of Nitrated Fibroin. TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1915, **37**, 2598—2603).—Johnson and Kohmann (A., 1915, i, 899, 1060) have shown that the nitrotyrosine obtained by Strecker in 1850 by the direct nitration of tyrosine is a mixture of *o*-nitrotyrosine, m. p. 231° (decomp.), with the meta-isomeride, the former being the chief product. The nitrotyrosine prepared by Inouye (A., 1912, i, 922) by the hydrolysis of nitrated silk fibroin is now proved to be identical with the synthetic *o*-nitrotyrosine, the identity being demonstrated by direct comparison and by conversion of both with ammonium thiocyanate and acetic anhydride into 2-thio-4-*m*-nitro-*p*-hydroxybenzylhydantoin. The two fractions, m. p. 216° and 233° respectively, obtained by Inouye were both of *o*-nitrotyrosine, the second fraction being the purer.

D. F. T.

Steric Hindrance. G. REDDELIEN (*Ber.*, 1915, **48**, 1462—1472).—Great caution is required in drawing conclusions as to the chemical affinity of a substance from its rate of reaction, because the rate of reaction may be very different for compounds of approximately equal affinity towards the same reagent (compare Reddelien, A., 1915, i, 257). Classes of compounds suited to the illustration of this point are the additive compounds of various aromatic ketones with nitric acid, and the ketone anils.

Thus benzophenone, phenyl *p*-tolyl ketone, phenyl *o*-tolyl ketone, and phenyl mesityl ketone combine slowly with nitric acid (D 1·40) at the ordinary temperature, forming compounds of the type

$CRR'O,HNO_3$, the derivatives of the first two ketones having respectively m. p. 59—60° and 30—31°, whilst those of the third and fourth are oily. Hydrolysis by water effects an almost complete fission of these compounds into their components, but the reaction is reversible, and if diluted nitric acid is used two layers are obtained, the upper consisting of a mixture of the ketone and ketone-nitrate, whilst the lower layer is almost pure nitric acid. By determining the content of nitric acid in the upper layer, after equilibrium is reached, the degree of hydrolysis of the ketone-nitrate can be calculated, and it is found that the results are comparable for the whole class, nitric acid (D 1·362) hydrolysing approximately 20—25%, whilst acid of D 1·326 hydrolyses approximately 35—40%. By shaking the pure ketones with acid of these respective strengths, the reversibility of the reaction can be demonstrated, although the final equilibria do not quite coincide with those obtained by hydrolysis with the corresponding acid, possibly owing to the difference in the conditions caused by the formation of some free nitric acid during the hydrolysis and the removal of some acid during the synthetic process. These ketones therefore exhibit comparable affinity towards nitric acid, but the rate of combination varies widely, benzophenone being most rapid and phenyl mesityl ketone most sluggish.

A similar investigation was also made with benzophenoneanil, benzophenone-*p*-tolil, benzophenone-*m*-tolil, *benzophenone-o-tolil*, $CPh_2{:}N{\cdot}C_6H_4Me$ (yellow needles, m. p. 50—51°), *phenyl p-tolyl ketone anil*, $C_6H_4Me{\cdot}CPh{:}NPh$ (a yellow oil, b. p. 233°/13 mm.), phenyl *o*-tolyl ketone anil, and *benzophenone mesil*,

$$CPh_2{:}N{\cdot}C_6H_2Me_3$$

(deep yellow plates, m. p. 68°). When the constituents of these compounds are heated with a little of the corresponding amine hydrobromide (Reddelien, A., 1914, i, 695) for thirty to forty-five minutes, equilibrium mixtures are obtained containing 63—71% of the condensation product. The rate of reaction, however, differs immensely, and comparisons can be made by noting the respective times required for the disappearance of the colour of an alcoholic solution to which a definite amount of hydrochloric acid has been added; the anils have a decided colour, especially in the presence of the acid, whilst the products of fission are colourless. The effect of the ortho-substituents is most marked, whereas that of a meta- or para-substituent is very slight. This result appears to confirm the views of Pfeiffer (A., 1911, i, 788), who has suggested that in the hydrolysis of an anil addition of water occurs primarily at the carbon atom of the $\cdot C{:}N\cdot$-group. D. F. T.

Configuration of the Two Oximes of Phenyl α-Naphthyl Ketone. MARIO BETTI and AMOS BECCIOLINI (*Gazzetta*, 1915, **45**, ii, 219—224).—When subjected to the Beckmann rearrangement by treatment with phosphorus pentachloride, the unstable oxime, m. p. 127°, of phenyl α-naphthyl ketone (compare Betti and Poccianti, A., 1914, i, 550) is converted into the α-naphthalide of benzoic acid, and has, therefore, configuration I. Similarly, the stable

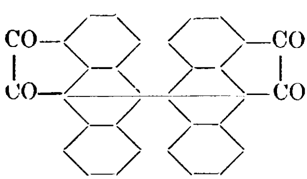
oxime, m. p. 161°, yields the anilide of α-naphthoic acid, and consequently corresponds with formula II (compare also Poccianti, A., 1915, i, 822):

$$\begin{array}{c} C_{10}H_7\cdot \underset{\Vert}{C}\cdot C_6H_5 \\ HO\cdot N \\ \text{(I.)} \end{array} \qquad\qquad \begin{array}{c} C_{10}H_7\cdot \underset{\Vert}{C}\cdot C_6H_5 \\ N\cdot OH \\ \text{(II.)} \end{array}$$

T. H. P.

Action of Oxalyl Chloride on Dianthryl. C. Liebermann, M. Kardos, and G. Mühle (*Ber.*, 1915, **48**, 1648—1653).—The reaction by which anthracene was converted into aceanthrenequinone and anthracene-9-carboxylic acid (A., 1911, i, 202) has been applied to dianthryl. It is found that the nuclei are not severed, but that the chief product is a diquinone, mixed with related carboxylic acids, which can be separated by reason of solubility differences. Compared with the analogous anthracene derivatives (*loc. cit.*, and A., 1911, i, 387; 1913, i, 883) the new compounds are deeper in colour.

Diantbryl, obtained by the reduction of anthracene with tin and a solution of hydrogen chloride in glacial acetic acid, was stirred in the cold with oxalyl chloride, aluminium chloride, and carbon disulphide. The black product was decomposed by water, freed from the solvent, and then boiled with dilute hydrochloric acid. The insoluble residue was then boiled with 5% sodium carbonate, which dissolved the small amount of acids, and the remaining ketone was finally dissolved by a hot solution of sodium hydrogen sulphite, reprecipitated by sulphuric acid, and crystallised from a large volume of benzene.



Bisanthrylacediquinone (10:10′-*diaceanthrenediquinone*), annexed formula, is a bright red powder, m. p. above 350°, which forms a yellow oxime and a dark red phenylhydrazone.

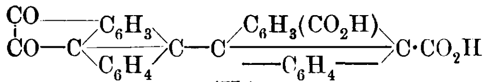
The mixture of acids obtained by acidifying the above sodium carbonate extract was warmed with a suspension of calcium carbonate in water. This gave a solution of a *calcium* salt, from which *dianthryltetracarboxylic acid*, annexed formula, was isolated

$$CO_2H\cdot C \begin{array}{c} \diagup C_6H_3(CO_2H) \diagdown \\ \diagdown\text{——}C_6H_4\text{——}\diagup \end{array} C—C \begin{array}{c} \diagup C_6H_3(CO_2H) \diagdown \\ \diagdown\text{——}C_6H_4\text{——}\diagup \end{array} C\cdot CO_2H,$$

as an orange powder, which loses water at above 110°. The remaining acids were liberated from the insoluble calcium salts and extracted with boiling glacial acetic acid. This dissolves *diaceanthrenequinonemonocarboxylic acid* (I), a brick-red powder, leaving the *dicarboxylic acid* (II), which has a chocolate colour.

$$\begin{array}{l} CO\text{———}\diagup C_6H_3 \diagdown \qquad \diagup C_6H_4 \diagdown \\ \vert \\ CO—C \qquad\quad C—C \qquad\quad C\cdot CO_2H \\ \qquad \diagdown C_6H_4 \diagup \qquad \diagdown C_6H_4 \diagup \end{array}$$

(I.)

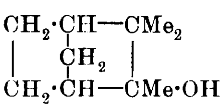


(II.)

J. C. W.

The Benzylidenementhones. EYVIND BŒDTKER (*Bull. Soc. chim.*, 1915, [iv], **17**, 374—380. Compare Martine, A., 1904, i, 903).—The benzylidenementhone hydrochloride, m. p. 140°, obtained by Wallach (A., 1899, i, 532), when acted on by aluminium chloride in benzene solution, yields the diphenylmenthylmethane, m. p. 160·5—161·5° (compare A., 1907, i, 857). The original menthone derivative must therefore have the constitution $C_8H_{16}<\begin{matrix}CH\cdot CHPhCl\\ CO\end{matrix}$ (compare Martine, *loc. cit.*). A small amount of an isomeric diphenylmenthylmethane, m. p. 135—136°, was also obtained, and was considered as coming from the oily isomeride of the starting material, which was found to be present to the extent of 25%. This oil when isolated and acted on in alcoholic solution by potassium yielded a *benzylidenementhone*, b. p. 189°/12 mm., which is a stereoisomeride of the two benzylidenementhones obtained by Martine (*loc. cit.*). This compound is a bright yellow liquid, D_4^{19} 1·0105; n_D^{20} 1·5403; $[\alpha]_D^{21}$ $-82°23'$ in benzene solution. With hydrochloric acid in acetic acid solution, it yielded the original oily compound, and with potassium cyanide in alcoholic solution, it yielded a number of isomeric cyano-derivatives, $C_8H_{16}<\begin{matrix}CH\cdot CHPh\cdot CN\\ CO\end{matrix}$ With hydroxylamine, it gave an additive product, m. p. 160°, identical with that obtained by Martine from its isomerides (*loc. cit.*). With magnesium phenyl bromide in ethereal solution, it gave a diphenylmenthylmethane, m. p. 156—157°, stereoisomeric with the two mentioned above. W. G.

Determination of Constitutions in the Camphene Group. VI. Isomerism of Methylcamphenilol and Camphene Hydrate. OSSIAN ASCHAN (*Annalen*, 1915, **410**, 222—239. Compare A., 1910, i, 709; 1911, i, 794, 796, 797; 1913, i, 886).—Since the conversion of camphene through the hydrochloride into camphene hydrate is effected without change in the camphene skeleton (A., 1911, i, 794), the structure of the hydrate must be represented by the annexed formula. This is the same as that ascribed by Moycho and Zienkowski (A., 1905, i, 654) to methylcamphenilol. The two substances, however, are certainly not identical, and are therefore to be regarded as stereoisomerides.



Attempts to detect camphene hydrate in the preparation of methylcamphenilol from camphenilone and magnesium methyl iodide have not been successful.

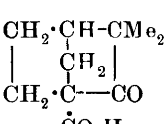
Camphene hydrochloride, prepared from camphene and ethereal hydrogen chloride at the ordinary temperature or in the cold, or from borneol or *iso*borneol and phosphorus pentachloride, yields the same camphene hydrate by treatment with milk of lime;

methylcamphenilol is not formed in any case. Camphene hydrochloride, bornyl chloride, and *iso*bornyl chloride, therefore, are identical substances.

Camphene hydrate yields a *phenylurethane*, $C_{17}H_{23}O_2N$, crystals, m. p. 89°, and by boiling with acetic anhydride and anhydrous sodium acetate is partly decomposed into camphene and water and partly esterified, the resulting *acetate*, $CH_3{\cdot}CO{\cdot}O{\cdot}C_{10}H_{17}$, b. p. 103—105°/14 mm., D_{15}^{15} 0·9852, yielding a mixture, probably of camphene hydrate and *iso*borneol, by hydrolysis. Methylcamphenilol, complete directions for the preparation of which from magnesium methyl iodide and camphenilone (m. p. 41—41·25°; $[\alpha]_D^{18 \cdot 5}$ +30·05° in 50·46% absolute alcoholic solution) and its purification are given, has m. p. 96° (Moycho and Zienkowski, *loc. cit.*, give 117—118°) and $[\alpha]_D^{21}$ +12·7° in 47·47% alcoholic solution. Its phenylurethane has m. p. 126°. When heated with acetic anhydride, methylcamphenilol is mainly converted into an acetate, b. p. 100—102°/11 mm., D_4^{18} 1·003, $[\alpha]_D$ +18·9°, and, unlike camphene hydrate, is not decomposed into camphene and water to any great extent. Similarly, methylcamphenilol is only slightly attacked by boiling glacial acetic acid and sodium acetate, whilst camphene hydrate is almost completely converted into camphene.

The following simple test is given for distinguishing between borneol, *iso*borneol, methylcamphenilol, and camphene hydrate. The alcohol, 0·5 gram, dissolved in the cold in 0·5 c.c. of glacial acetic acid, is treated with about 0·05 gram of 50% sulphuric acid, and the solution is heated to visible boiling for not more than about ten seconds, and is at once cooled to 10°. Borneol only dissolves in the boiling liquid, and at once crystallises on cooling. The solution of *iso*borneol becomes distinctly turbid at 10°, and clarifies again at 18—20°. The solution of methylcamphenilol does not become turbid on cooling, whilst that of camphene hydrate is turbid even while boiling, and yields two distinct phases on cooling. C. S.

Determination of Constitutions in the Camphene Group. VII. Camphenonic Acid and its Optically Active Components. OSSIAN ASCHAN (*Annalen*, 1915, **410**, 240—256. Compare preceding abstract).—[With W. FORSMAN.]—*dl*-Camphenonic acid, formerly obtained by the dry distillation of *dl*-camphenic acid (A., 1911, i, 797), is now prepared in better yield by boiling the acid with acetic anhydride and subsequently distilling in a current of carbon dioxide. It does not form a semicarbazone, but yields an *oxime*, crystals containing C_6H_6, m. p. 173°. The acid does not form a benzylidene derivative, is not attacked by chromic and acetic acids or alkaline permanganate, and reacts only slowly with a boiling mixture of 1·42 and 1·5 nitric acids; its formula is therefore most probably that annexed.



The acid is reconverted into *dl*-camphenic acid by boiling alcoholic sodium ethoxide. It forms an *ethyl* ester, $C_{12}H_{18}O_3$, and *amide*, four-sided plates or leaflets, m. p. 184—185°, and is converted by sodium and boiling ethyl alcohol partly into camphenic acid by hydrolysis and partly

into dl-*camphenolic acid*, $C_9H_{14}(OH)\cdot CO_2H$, large, monoclinic prisms, m. p. 99—100°, by reduction.

[With R. COLLANDER.]—When the camphene used for the preparation of camphenic acid is relatively strongly dextrorotatory, the latter yields by dehydration, in addition to *dl*-camphenonic acid, a small quantity of d-*camphenonic acid*, needles containing $1H_2O$, m. p. 70° or 105—106° (anhydrous), $[\alpha]_D^{20}$ +79·1° in absolute alcohol, which forms a *chloride*, m. p. 40—45°, and an *amide*, plates, m. p. 152·5—154°, $[\alpha]_D^{20}$ +56·6° in alcohol, and is converted into *d*-camphenic acid by fusion with potassium hydroxide. l-*Camphenonic acid*, prepared in a similar manner to the *d*-acid, the initial material being a strongly lævorotatory camphene, resembles its *d*-isomeride in the magnitudes of its physical constants; the l-*amide* has m. p. 152·5—154° and $[\alpha]_D^{20}$ −58·3° in alcohol. A solution in water of equal weights of the *d*- and *l*-acids yields *dl*-camphenonic acid by crystallisation; a mixture of the active amides yields the racemic amide. C. S.

Camphorated Chloral. D. E. TSAKALOTOS (*J. Pharm. Chim.*, 1915, [vii], **12**, 355—358).—Camphorated chloral is prepared by mixing equal weights of camphor and chloral. It is a very viscid liquid.

The melting point of mixtures of camphor and chloral containing increasing quantities of camphor is gradually lowered until the mixture is liquid at the ordinary temperature and contains about 40% of camphor. By the further addition of camphor (until the mixture contains 65% of camphor) another point is reached beyond which the mixture remains solid with an increasingly high melting point until the melting point of pure camphor (176°) is reached. The occurrence of this region of great viscosity is considered by the author to indicate the existence of a definite compound of the two substances. H. W. B.

Composition of Wood Turpentine. MAXWELL ADAMS (*J. Ind. Eng. Chem.*, 1915, **7**, 957—960).—Almost all the constituents of the oleo-resin of three varieties of West American pine examined, *Pinus ponderosa*, *P. Jeffreyi*, and *P. monophylla*, were found in the wood turpentine of the corresponding wood. The oil from the wood of *P. monophylla*, obtained by distillation on an oil-bath under diminished pressure, had the following constants: D^{15} 0·9702, n_D^{15} 1·4771, $[\alpha]_D^{20}$ +21·15°, and α-pinene, β-pinene, and cadinene were identified in it. The volatile oil from Jeffrey pine-wood contained 90—95% of *n*-heptane, together with traces of limonene and possibly citronellal. The oil from yellow pine-wood, *P. ponderosa*, had D^{15} 0·8626, n^{15} 1·4727, $[\alpha]_D$ −13·15°. Limonene and α- and β-pinene were identified in it, and on fractionation it behaved very similarly to the oil obtained from the oleo-resin. G. F. M.

Norwegian Oil of Turpentine. H. W. FOSSE (*Ber. Deut. pharm. Ges.*, 1915, **25**, 303—313).—The author has examined the oil obtained by boiling the woody roots of the pine and the fir with so-called sulphite liquor under 6—8 atmos. The crude oil is yellowish-

brown, has b. p. 157—160°, D^{15} 0·8918, $[\alpha]_D^{20}$ +7·8°, and contains terpenes, sesquiterpenes, resins, and sulphur compounds belonging to the mercaptan series; the last, which are probably produced during the process of manufacture, can be almost entirely removed by treatment with bleaching-powder and hydrochloric acid. *d*-Pinene and sylvestrene have been identified; the presence of cadinene has not been established with certainty. C. S.

Definition, Classification, and Evaluation of Caoutchoucs. I. Two New Constants of Caoutchoucs. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1374—1401).—The elastic properties of caoutchoucs and their property of becoming vulcanised when treated with sulphur are associated, not merely with natural caoutchouc, but with a more or less typical state of matter, to which the author gives the name of the "elastic" or "caoutchouc" state. This condition is exhibited only by amorphous compounds of high molecular weight and colloidal properties, and its degree of stability varies widely with substances of different composition and structure. To substances capable of existing in this elastic state the name "resinoids" (in Russian, rezina = caoutchouc) is given. The elastic condition of matter exists only over a definite interval of temperature; thus, below −20° natural caoutchouc loses its elastic properties and becomes leathery. To the temperature at which a substance is transformed into the elastic condition the name "temperature of elasticity" is given, and to the temperature at which the elastic properties are completely lost the name "fatal temperature." These temperatures vary with the composition and structure of the caoutchouc, and are affected by admixture of extraneous substances, the former being higher than the latter temperature with all resinoids; both temperatures are altered by vulcanisation. All caoutchoucs obtained by direct heating of βγ-dimethylerythrene at temperatures between 50° and 170°, in presence or absence of a catalyst, exhibit one and the same temperature of elasticity. Depression or elevation of the temperature of elasticity of any given caoutchouc is accompanied by a corresponding change in the fatal temperature.

A caoutchouc with which the temperature of elasticity, the fatal temperature, and the interval between these agree approximately with the corresponding constants for natural caoutchouc is termed a "normal" caoutchouc. Simple resinoid is the name given to a homogeneous caoutchouc-like substance, of which the principal part consists of one and the same compound. A complex resinoid, on the other hand, is formed of a mixture of substances of different composition or structure, each of which separately may have nothing in common with caoutchouc. Harries has suggested that a caoutchouc be termed normal if the products yielded when its ozonide is decomposed by water are the same as those obtained from the ozonide of Para caoutchouc, but Steimmig (A., 1914, i, 307) found that, unlike the ozonide of Para caoutchouc, the ozonides of all synthetic caoutchoucs yet obtained from isoprene give, when decom-

posed with water, acetonylacetone and succinic acid in addition to lævulinaldehyde.

Only caoutchoucs which, according to the author's definition, are normal and stable are of wide applicability in practice. Regenerated caoutchouc, prepared by treatment of old rubber with alkali, is a typical abnormal caoutchouc with a temperature of elasticity lying above 100°, and varying with the conditions of the regeneration and vulcanisation and with the condition of the original waste rubber used. Up to the present time no means have been discovered of converting regenerated caoutchouc into normal caoutchouc. The following caoutchoucs are abnormal: those obtained by polymerisation of isoprene in presence of an alkali metal with or without barium peroxide, those obtained by isomerisation, and all the known polymerides of $\beta\gamma$-dimethylethylerythrene. Normal caoutchoucs are: erythrene-caoutchoucs, obtained either by the action of zinc dust on caouprene bromide or by the action of an alkali metal on erythrene; isoprene-caoutchoucs obtained in small yield by direct heating of isoprene, or by the action of an organic or inorganic peroxide, or by the action of a peroxide followed by that of an alkali metal; those obtained by the simultaneous action of barium peroxide and sodium on β-myrcene. The properties of an ideal caoutchouc are outlined. T. H. P.

Two New Constants for Caoutchoucs: Elasticity Point and Fatal Temperature. I. I. Ostromisslenski and (Mlle.) I. M. Kelbasinskaja (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1401—1441. Compare preceding abstract).—The elasticity point is defined as the temperature at which the temperature curves of the different properties characterising the elastic condition of a caoutchouc cease to be analytical curves. This temperature and the fatal temperature represent characteristic constants for resinoids, and in particular for caoutchoucs, similar to the melting point of a crystalline solid or the boiling point of a liquid. These temperatures may be measured in colloidal solutions, and, unlike viscosity, surface tension, etc., they do not change with lapse of time and do not depend on the nature of the solvent. The elasticity point and the fatal temperature of a solution of caoutchouc may be determined by means of either the viscosity, or the density, or the surface tension at different temperatures, all three methods giving perfectly identical results; an apparatus is described by means of which the viscosity and surface tension may be measured simultaneously. The presence of foreign substances and the nature of the solvent are not reflected in the elasticity point and the fatal temperature of caoutchouc solutions if the final condition of aggregation of the solvent and the concentration of the solution at the experimental temperature remain unchanged. These two temperatures serve to identify or differentiate caoutchoucs and furnish a basis for the more rational classification of caoutchoucs and caoutchouc-like compounds. There is evidence in support of the assumption that these temperatures represent, for colloids in general and not merely for caoutchoucs, the first constants which are invariable

with reference to time. The paper contains a considerable mass of data relating to the physical constants of solutions of various caoutchoucs in different solvents. T. H. P.

Bixin. I. J. RINKES (*Chem. Weekblad*, 1915, **12**, 996—1000).—The empirical formula of bixin is $C_{27}H_{32}O_4$. On ozonisation, methylbixin yields an *ozonide*, from which methylglyoxal has been isolated. A. J. W.

Physiological Theory of Chlorophyll. E. G. PRINGSHEIM (*Ber. Deut. bot. Ges.*, 1915, **33**, 379—385).—A discussion of Ivanovski's paper (A., 1915, i, 705). N. H. J. M.

Azafrin. III. C. LIEBERMANN and G. MÜHLE (*Ber.*, 1915, **48** 1653—1660. Compare A., 1913, i, 889).—Azafrin has now been converted into an iodide and reduced to an oil by catalytic means, but neither product agrees with the formula, $C_{31}H_{42}O_5$, which has been assigned to the pigment. Since the compounds with acids on which much had been based are unstable and amorphous, and all the substances are difficult to burn, the question of a formula is left open again.

Azafrin gives a greenish-black *compound* with formic acid, which dissolves in acetic acid with a deep violet colour. When the hydrochloric acid compound is treated with an alkali, it gives a chlorine-free, colourless substance, which may be related to a pale yellow *compound* which is obtained by boiling azafrin with glacial acetic acid or dimethylaniline. The *iodide*, obtained by the addition of iodine in a benzene solution, crystallises in almost black, stout columns, m. p. 145° (decomp.), which dissolve in chloroform or alcohol with deep blue or violet colours. The colour is destroyed by sulphurous acid, but reappears on boiling off the agent. The reduction *product*, obtained by catalytic means, is a colourless oil which corresponds best with $C_{31}H_{54 \text{ or } 56}O_5$, and methylazafrin gives a similar *substance*, $C_{32}H_{58 \text{ or } 60}O_5$. Bixin behaves in the same way on reduction, but does not form an iodide. J. C. W.

A Chemical Paradox. O. DE VRIES (*Chem. Weekblad*, 1915, **12**, 1000—1001).—The intense violet-red coloration produced with methyl-orange by deliquesced zinc chloride is not due to acidity of the solution, but to the formation of a complex red derivative. This explains the apparent paradox that the red solution seems to be neutralised (yellow) by addition of acid and then acidified (red) by addition of excess of acid. A. J. W.

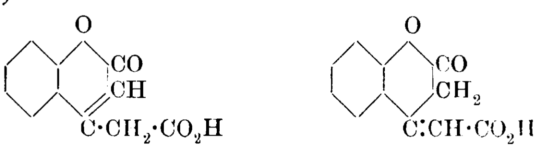
The Newer Theories of Tanning. R. LAUFFMANN (*Kolloid Zeitsch.*, 1915, **17**, 37—44).—A review of recent theories of the nature of the tanning process, in which a comparison is made between the theories which ascribe the action to chemical changes and those in which the tanning is attributed to physical changes. A feature common to both groups is that the active agents are assumed to be colloidal substances, or, at any rate, substances of high molecular weight. H. M. D.

3-Methylcoumarin. H. SIMONIS [with GOLDENZWEIG] (*Ber.*, 1915, **48**, 1583—1585).—Von Pechmann has shown (1884) that phenols with a second hydroxyl group in the meta-position, such as resorcinol and orcinol, condense readily with malic acid under the influence of concentrated sulphuric acid to form coumarins, but that phenol itself gives no weighable quantity of coumarin. The present author found that it was sometimes advisable to use diluted sulphuric acid in these coumarin syntheses (A., 1908, i, 339), and has therefore applied his 73% acid to the condensation of phenol with malic and α-methylmalic acids. The yields are found to be improved, but are still far from satisfactory, being 1 gram of coumarin from 37 grams of malic acid and 1·5 grams of 3-methylcoumarin from 80 grams of α-methylmalic acid. J. C. W.

The Coumarin Condensation. BIMAN BIHARI DEY (T., 1915, **107**, 1606—1651).—The condensation of phenols with acetonedicarboxylic acid, ethyl oxalacetate, β-ketonic esters, ethyl α-chloro-oxalacetate, and ethyl sodiomalonate has been thoroughly investigated. The products obtained in all the cases, with the exception of the ketonic esters, were derivatives of coumarin-4-acetic acid. The methods by which the constitutions of these are determined are discussed, as well as the action of alkalis on them. Most of the acids seem to exist in two forms; the first apparently changes into the second on keeping or on boiling with a solvent, but it cannot be regenerated from the ultimate product. As space isomerism ideas cannot apply to these cases, it is suggested that the first product is a mixture of two forms, one of which is labile. Thus, in the case of acetonedicarboxylic acid, this in the enolic form

$$CO_2H\cdot CH{:}C(OH)\cdot CH_2\cdot CO_2H + C_6H_5\cdot OH$$

may react in two ways and would give two different coumarins (I and II):



(I.) (II.)

The form II would change into I on heating in a solvent. This involves the assumption of a mobile hydrogen atom in the system $\cdot CH_2\cdot C{:}CH\cdot$, and such has been advocated in the case of the very closely allied glutaconic acid systems $\cdot CO\cdot CH_2\cdot CH{:}CH\cdot CO_2H$ and $\cdot CO\cdot CH{:}CH\cdot CH_2\cdot CO_2H$ (Thorpe, T., 1911, **99**, 2188).

Derivatives of α-Naphthol.—An intimate mixture of α-naphthol and acetonedicarboxylic acid was carefully dissolved in concentrated sulphuric acid, and next day the mass was poured into ice-water. The crude product had m. p. 212—213°, but the 1:2-*α-naphthapyrone-4-acetic acid*, $\begin{matrix} O\cdot CO\cdot CH \\ C_{10}H_6\cdot C\cdot CH_2\cdot CO_2H \end{matrix}$, obtained after boiling with alcohol or acetic acid, formed slender, yellow plates, m. p. 181°. Both substances lost carbon dioxide at higher temperatures.

yielding 4-methyl-1 : 2-α-naphthapyrone. The acid was converted into an *ethyl* ester, clusters of long needles, m. p. 139°, an *anilide*, short, green prisms, m. p. 264° (decomp.), an *amide*, aggregates of hard prisms, m. p. 262°, and also nitrated to 6-*nitro*-1 : 2-α-*naphthapyrone*-4-*acetic acid*, $C_{15}H_9O_6N$, yellow nodules, m. p. 212°. The latter compound changed into 6-*nitro*-4-*methyl*-1 : 2-α-*naphthapyrone*, $C_{14}H_9O_4N$, at its m. p., and this was also prepared by nitrating 4-methyl-1 : 2-α-naphthapyrone. This nitro-compound was boiled with sodium hydroxide solution, when the pyrone ring was opened and β-4-*nitro*-1-*hydroxy*-2-*naphthylcrotonic acid*,

$$NO_2\cdot C_{10}H_5(OH)\cdot CMe\colon CH\cdot CO_2H,$$

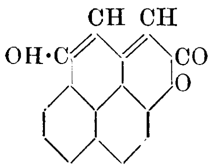
was formed, which gave a *sodium* salt, deep red needles, and melted and lost water again at 128—130°. The nitro-compound was also oxidised by alkaline permanganate to 4-nitro-1-naphthol-2-carboxylic acid, m. p. 214° (decomp.), and it was further reduced to 6-*amino*-4-*methyl*-1 : 2-α-*naphthapyrone*, $C_{14}H_{11}O_2N$, long, yellow, lustrous needles, m. p. 243°; *hydrochloride*, decomp. 276—278°, *acetyl* derivative, soft, colourless needles, m. p. 277—278°, *benzoyl* derivative, clusters of long needles, m. p. 261—262°. The methylnaphthapyrone was also boiled with phosphorus pentasulphide and xylene, when 2-*thio*-4-*methyl*-1 : 2-α-*naphthapyrone*,

$$C_{10}H_6{<}\begin{matrix}O\text{---}CS\\ CMe\colon CH\end{matrix},$$

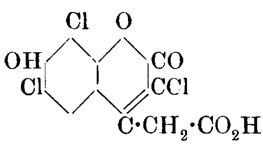
was obtained in small, yellow prisms with green reflex, m. p. 187°. This was desulphurised by boiling with mercuric oxide in benzene, and was also converted into the *oxime* of 4-methyl-1 : 2-α-naphthapyrone, soft, yellow needles, m. p. 235°. In the same way the ethyl ester of the original acid was transformed into *ethyl* 2-*thio*-1 : 2-α-*naphthapyrone*-4-*acetate*, $C_{17}H_{14}O_3S$, deep golden-yellow needles, m. p. 146°.

Derivatives of β-Naphthol.—Acetonedicarboxylic acid condensed with β-naphthol to form 4 : 3-β-*naphthapyrone*-1-*acetic acid*, $C_{15}H_{10}O_4$; the first precipitate had m. p. 202—203°, but the recrystallised acid, yellow needles, melted and changed into 1-methyl-4 : 3-β-naphthapyrone at 191°. The *silver* salt, *methyl* ester, pale yellow plates, m. p. 187°, and *ethyl* ester, colourless plates, m. p. 164°, were prepared. The acid was hydrolysed by boiling with sodium hydroxide, to β-2-*hydroxy*-1-*naphthylglutaconic acid*, $CO_2H\cdot CH_2\cdot C(C_{10}H_6\cdot OH)\colon CH\cdot CO_2H$, a yellow powder with an agreeable odour, which melts at 174° and changes into 1-methyl-4 : 3-β-naphthapyrone. The latter substance was converted into 2-*thio*-1-*methyl*-4 : 3-β-*naphthapyrone*, $C_{14}H_{10}OS$, yellow sheaves, m. p. 199°, and this gave the *oxime* of 1-methyl-4 : 3-β-naphthapyrone, $C_{14}H_{11}O_2N$, lemon yellow needles, m. p. 197°. 2-*Chloro*-1-*methyl*-4 : 3-β-*naphthapyrone*, $C_{10}H_6{<}\begin{matrix}CMe\colon CCl\\ O\text{---}CO\end{matrix}$, m. p. 135°, was prepared by chlorination or by condensing β-naphthol with ethyl α-chloroacetoacetate. The 1-methyl-4 : 3-β-naphthapyrone was hydrolysed by alcoholic potassium hydroxide to β-2-*hydroxy*-1-*naphthylcrotonic acid*, $OH\cdot C_{10}H_6\cdot CMe\colon CH\cdot CO_2H$, colourless plates, m. p. 146° (loss

of H_2O), and the chloro-derivative was hydrolysed to *α-chloro-β-2-hydroxy-1-naphthylcrotonic acid*, m. p. 148°. The ethyl ester of the original 4 : 3-β-naphthapyrone-1-acetic acid suffered condensation in concentrated sulphuric acid at 120—130° to *5-hydroxy-2-keto*peri-peri-*naphthindenofuran*, annexed formula. This crystallised in soft, yellow needles, m. p. 280—282° (decomp.), exhibited intense green fluorescence in alcohol, and gave a *sodium* salt, orange-red prisms, an *acetate*, short, yellow needles, m. p. 211—212°, a *benzoate*, clusters of soft needles, m. p. 207°, and a *methyl ether*, m. p. 224—229°.



Derivatives of Resorcinol.—Freshly prepared 7-hydroxycoumarin-4-acetic acid (Burton and Pechmann, A., 1891, 672) has m. p. 209—210°, but the recrystallised substance has m. p. 201°. On boiling with alkalis, it changes into β-2 : 4-dihydroxyphenylglutaconic acid, the *disilver* salt of which is yellow. Ethyl 7-hydroxycoumarin-4-acetate was obtained in the usual way or by the condensation of resorcinol with ethyl sodiomalonate. It has m. p. 157°, and yields an *acetyl* derivative, $C_{15}H_{14}O_6$, soft, snow-white needles, m. p. 124°, and a *benzoate*, long needles, m. p. 126°. *Methyl 7-methoxycoumarin-4-acetate*, $C_{13}H_{12}O_5$, was prepared by the action of methyl sulphate. It formed rosettes of silky needles, m. p. 122°, and was hydrolysed to *7-methoxycoumarin-4-acetic acid*, slender prisms, m. p. 187°; *ethyl* ester, m. p. 105°. This acid was also obtained by condensing resorcinol monomethyl ether with acetonedicarboxylic acid, and it changed on melting into 7-methoxy-4-methylcoumarin, m. p. 159°. *3 : 6 : 8-Trichloro-7-hydroxycoumarin-4-acetic acid*, annexed formula, was prepared by direct chlorination. It changed on melting, m. p. 246°, into 3 : 6 : 8-trichloro-7-hydroxy-4-methylcoumarin (Fries and Lindemann, A., 1914, i, 570), and was transformed by boiling with alcoholic potassium hydroxide into *4 : 6-dichloro-5-hydroxy-1-carboxycoumarone-2-acetic acid*,



$$OH\cdot C_6HCl_2{<}\begin{matrix}O\cdot C\cdot CO_2H\\ \|\\ —C\cdot CH_2\cdot CO_2H\end{matrix},$$

long needles, m. p. 256—257° (decomp.).

Derivatives of Quinol.—Quinol reacted feebly with acetonedicarboxylic acid, better with the ester, giving *ethyl 6-hydroxycoumarin-4-acetate*, $C_{13}H_{12}O_5$, which crystallised in fern-like needles, m. p. 174—176°.

Derivatives of Catechol.—A very small yield of *8-hydroxycoumarin-4-acetic acid*, $C_{11}H_8O_5$, short needles, m. p. 228—230° (decomp.), was obtained by condensation with acetonedicarboxylic acid.

Derivatives of the Cresols.—The 7-methylcoumarin-4-acetic acid obtained from *m*-cresol (Fries and Volk, A., 1911, i, 204) yielded the *anilide*, blunt needles, m. p. 250°, and *3 : 6-dichloro-7-methylcoumarin-4-acetic acid*, $C_{12}H_8O_4Cl_2$, colourless plates, which changed

on fusion, m. p. 231—232°, into 3 : 6-*dichloro*-4 : 7-*dimethylcoumarin*, needles, m. p. 214°. The latter was synthesised, for comparison, from chlorocresol and ethyl α-chloroacetoacetate. *p*-Cresol was converted into 6-*methylcoumarin*-4-*acetic acid*, long needles, m. p. 181° (changing into 4 : 6-dimethylcoumarin, m. p. 148°); *ethyl* ester, silky needles, m. p. 131°, *anilide*, m. p. 242—243°. The acetic acid was chlorinated, and the 3-*chloro*-6-*methylcoumarin*-4-*acetic acid* so obtained formed silvery needles, m. p. 163—164° (changing into 3-chloro-4 : 6-dimethylcoumarin, m. p. 159°), and yielded 1-*carboxy*-4-*methylcoumarone*-2-*acetic acid*, m. p. 244° (*silver* salt) on boiling with alcoholic potassium hydroxide. *o*-Cresol was condensed with acetonedicarboxylic acid in the presence of alcohol to *ethyl* 8-*methylcoumarin*-4-*acetate*, $C_{14}H_{14}O_4$, m. p. 114°, from which the free *acid* was obtained in slender needles, m. p. 184° (changing into 4 : 8-*dimethylcoumarin*, $C_{11}H_{10}O_2$, m. p. 118°).

Derivatives of Orcinol.—5-*Hydroxy*-7-*methylcoumarin*-4-*acetic acid* was obtained in almost colourless needles, m. p. 260—265°, which changed into an *anhydride* at 150—160°, into β-2 : 6-dihydroxy-*p*-tolylglutaconic acid (*silver* salt) when boiled with alkalis, and into *p*-orsellinic acid on oxidation. The *ethyl* ester formed pale yellow, silky needles, m. p. 119°, and yielded a *sodium* salt, an *acetate*, soft needles, m. p. 139°, and a *benzoate*, colourless plates, m. p. 165°. On methylation with methyl sulphate, the acid gave *methyl* 5-*methoxy*-7-*methylcoumarin*-4-*acetate*, slender prisms, m. p. 133°; the free *acid*, $C_{13}H_{12}O_5$, formed colourless needles, m. p. 205° (changing into 5-methoxy-4 : 7-dimethylcoumarin, m. p. 144°).

Derivatives of o-4-*Xylenol*.—6 : 7-*Dimethylcoumarin*-4-*acetic acid*, $C_{13}H_{12}O_4$, was obtained in needles, m. p. 198° (changing into 4 : 6 : 7-trimethylcoumarin, m. p. 169°), and converted into the *ethyl* ester, m. p. 145°, the *anilide*, m. p. 259—260°, the 8-*nitro*-compound, pale yellow needles, m. p. 189—190°, and the 3-*chloro*-derivative, oblong plates, m. p. 194—196° (changing into 3-chloro-4 : 6 : 7-trimethylcoumarin). The ethyl ester was transformed into *ethyl* 2-*thio*-6 : 7-*dimethylcoumarin*-4-*acetate*, $C_{15}H_{16}O_3S$, orange needles, m. p. 156°.

Derivatives of Pyrogallol.—7 : 8-*Dihydroxycoumarin*-4-*acetic acid*, $C_{11}H_8O_6$, hard needles, changed into 7 : 8-dihydroxy-4-methylcoumarin (β-methyldaphnetin) on fusion, m. p. 214—215°. It gave an *anilide*, m. p. 270—272° (decomp.), and an *ethyl* ester, clusters of prismatic needles, m. p. 191° (*dibenzoate*, m. p. 128°). The ester was oxidised by lead peroxide to the quinone, *ethyl* 7 : 8-*diketocoumarin*-4-*acetate*, which formed dark red scales, m. p. 170—175° (decomp.). *Methyl* 7 : 8-*dimethoxycoumarin*-4-*acetate* was obtained in woolly needles, m. p. 139°, and hydrolysed to the *acid*, $C_{13}H_{12}O_6$, m. p. 179°.

Derivatives of Hydroquinol.—6 : 7-*Dihydroxycoumarin*-4-*acetic acid* formed short prisms, m. p. 214° (changing into 4-methylæsculetin, m. p. 264—265°), and gave an *ethyl* ester, stellar aggregates, m. p. 214°.

Derivatives of Phloroglucinol.—5 : 7-*Dihydroxycoumarin*-4-*acetic acid*, $C_{11}H_8O_6,H_2O$, was obtained in crystals, m. p. 204—205°, which

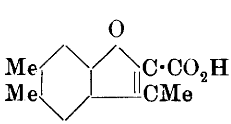
lost $2H_2O$ at 140—150°, forming an *anhydride*, and gave a crystalline *silver* salt.

Derivatives of Chlorophenols.—*p*-Chlorophenol gave a poor yield of *ethyl 6-chlorocoumarin-4-acetate*, $C_{13}H_{11}O_4Cl$, soft, silky needles, m. p. 167°, and this was hydrolysed to the *acid*, slender needles, m. p. 182° (changing into 6-chloro-4-methylcoumarin, m. p. 185°). 6-Chloro-*m*-cresol formed *6-chloro-7-methylcoumarin-4-acetic acid*, $C_{12}H_9O_4Cl$, white flakes, m. p. 206°, the *ethyl* ester of which crystallised in flat needles, m. p. 184°. The acid changed into *6-chloro-4:7-dimethylcoumarin*, m. p. 213°, on melting, and this was also synthesised by condensing chlorocresol with ethyl acetoacetate.

Derivatives of m-*Dimethylaminophenol.*—The phenol was heated with ethyl acetonedicarboxylate, alcohol, and anhydrous zinc chloride, and thus condensed to *ethyl 7-dimethylaminocoumarin-4-acetate*, $C_{15}H_{17}O_4N$, which dissolved in alcohol with an intense bluish-violet fluorescence, and crystallised in slender, colourless prisms, m. p. 133°. The ester was carefully hydrolysed to the *acid*, sheaves of yellow needles, m. p. 168° (changing into 7-dimethylamino-4-methylcoumarin, m. p. 145°).

Condensations with Oxalacetic Ester.—*p*-Cresol yielded *ethyl 6-methylcoumarin-4-carboxylate*, $C_6H_3Me<\begin{matrix}O\text{———}CO\\ C(CO_2Et):CH\end{matrix}$, m. p. 155—157°, which was hydrolysed to the *acid*, m. p. 208—210°. *p*-Chlorophenol gave *ethyl 6-chlorocoumarin-4-carboxylate*, bright yellow needles, m. p. 96—97°; free *acid*, pale yellow needles, m. p. 224°. 6-Chloro-*m*-cresol condensed to *ethyl 6-chloro-7-methylcoumarin-4-carboxylate*, golden-yellow needles, m. p. 117°; free *acid*, m. p. 246°. *m*-Cresol gave a small amount of *ethyl 7-methylcoumarin-4-carboxylate*, soft, pale yellow needles, m. p. 94—96°; free *acid*, m. p. 200°. β-Naphthol yielded *ethyl 4:3-β-naphthapyrone-4-carboxylate*, $C_{16}H_{12}O_4$, colourless prisms, m. p. 138°; free *acid*, m. p. 256°; white *silver* salt.

Condensations with Ethyl α-Chloroacetoacetate.—The ester was prepared by the action of sulphuryl chloride on ethyl acetoacetate, b. p. 105—110°/30 mm. *p*-Cresol gave *3-chloro-4:6-dimethylcoumarin*, $C_{11}H_9O_2Cl$, long, colourless needles, m. p. 160°. *m*-Cresol gave a much better yield of *3-chloro-4:7-dimethylcoumarin*, prismatic needles, m. p. 135°. *o*-4-Xylenol yielded *3-chloro-4:6:7-trimethylcoumarin*, long, colourless needles, m. p. 170°, which was converted into *2:4:5-trimethylcoumarilic acid*, annexed formula, m. p. 249—250° (decomp.), (*silver* salt), on boiling with alcoholic potassium hydroxide. This, and most coumarone derivatives, was found to give a violet solution in concentrated sulphuric acid, which became deep blue on warming.



Phloroglucinol yielded *3-chloro-5:7-dihydroxy-4-methylcoumarin*, yellow needles, m. p. 306—308° (decomp.), which gave a *dimethyl ether*, m. p. 170°, a *diacetate*, silvery needles, m. p. 154°, and a *dibenzoate*, rhombic plates, m. p. 187°. Hydroxyquinol gave a poor yield of *3-chloro-6:7-dihydroxy-4-methylcoumarin*, m. p. 259°, which formed a *diacetate*, m. p. 172°, and a *dibenzoate*, m. p. 193°.

α-Naphthol condensed to *3-chloro-4-methyl-1:2-α-naphthapyrone*, $C_{14}H_9O_2Cl$, long, stout needles, m. p. 225—227°.

Condensations with Ethyl α-Chloro-oxalacetate.—*m*-Cresol yielded *ethyl 3-chloro-7-methylcoumarin-4-carboxylate*, sharp, colourless needles, m. p. 154°, which changed into *5-methylcoumarone-1:2-dicarboxylic acid*, m. p. 218—221° (*silver* salt), on boiling with alcoholic potassium hydroxide. *o*-4-Xylenol gave *ethyl 3-chloro-6:7-dimethylcoumarin-4-carboxylate*, clusters of white needles, m. p. 177°, and this was converted into *4:5-dimethylcoumarone-1:2-dicarboxylic acid*, $C_{12}H_{10}O_5$, short needles, m. p. 321—324° (*silver* salt). The latter acid apparently gave 4:5-dimethylcoumarone on distillation with lime. J. C. W.

The Residual Affinities in Benzopyrones. H. Simonis and A. Elias (*Ber.*, 1915, **48**, 1499—1516).—After a survey of the various suggestions as to the structure of the compounds formed by pyrone derivatives with acids, the authors describe a series of additive compounds prepared from 2:3-dimethyl-γ-benzopyrone with various acids and salts. They find that the use of a neutral solvent, such as ether or alcohol, favours the formation of additive compounds containing molecular proportions of the components, whilst the products obtained with the use of acidic solvents are constituted otherwise, generally containing a bimolecular proportion of the γ-benzopyrone. The additive compounds undergo partial fission by water and complete fission by dilute aqueous acids.

Dimethyl-γ-benzopyrone reacts with cold concentrated hydrochloric acid, giving an unstable *hydrochloride*, represented by the formula $\begin{matrix} H_2O,C_{11}H_{10}O\colon O\cdot H \\ \qquad\qquad\qquad\quad | \\ H_2O,C_{11}H_{10}O\colon O\cdot Cl \end{matrix}$, colourless needles, m. p. 88°; if the base is allowed to combine with hydrogen chloride in ethereal solution the unstable *compound* produced has the composition $C_{11}H_{10}O\colon OHCl$, and crystallises in colourless needles. The *hydrobromide*, $C_{11}H_{10}O\colon OHBr$, colourless needles, m. p. 85—95°, and the *hydriodide*, $C_{11}H_{10}O\colon OHI$, yellow needles, were prepared by cooling a solution of the γ-benzopyrone in the corresponding concentrated aqueous acid.

With mercuric chloride in alcoholic solution the γ-benzopyrone reacts, giving colourless prisms, m. p. 188°, of a *compound*,

$$C_{11}H_{10}O\colon OCl\cdot HgCl,$$

but in concentrated hydrochloric acid the reaction gives rise to the compound $(C_{11}H_{10}O\colon OCl)_2Hg,HCl$, colourless prisms, m. p. 153—155°. By mixing their respective components in concentrated hydrochloric acid solution, the following dimethyl-γ-benzopyrone derivatives were prepared: *aurichloride*,

$$(C_{11}H_{10}O\colon OCl)_2AuCl,HCl,H_2O,$$

yellow needles, m. p. 161°; *platinochloride*,

$$(C_{11}H_{10}O\colon OCl)_2PtCl_2,2HCl,2H_2O,$$

yellow needles, decomp. at 192°; uranyl chloride *additive compound*, $(C_{11}H_{10}O\colon OCl)_2UO_2$, yellow prisms; *ferrichloride*,

$$(C_{11}H_{10}O\colon OCl)_2FeCl,HCl,$$

yellow needles, m. p. 116°, and $(C_{11}H_{10}O)_2FeCl_3$, yellow prisms.

Similarly in hydriodic acid solution there were prepared the additive *compounds*, $(C_{11}H_{10}O\colon OI)_2Cd,2HI,2H_2O$, pale yellow prisms, m. p. 103°, and $C_{11}H_{10}O\colon OI\cdot BiI_2,2HI,H_2O$, red needles or prisms, m. p. 220—223°.

In ethereal solution dimethylchromone and aniline condense together to form a *compound*, $(C_{11}H_{10}O\colon OH)_2NPh$, colourless prisms, m. p. 117°.

A dibromide of dimethyl-γ-benzopyrone has been described (Petschek and Simonis, A., 1913, i, 890), but hitherto it has been uncertain whether the bromine atoms are attached at the double bond or at the oxonium oxygen atom. When treated in ethereal solution with mercuric chloride, a *compound*,

$$(C_{11}H_{10}O\colon OCl)_2Hg,HBr,$$

colourless needles, m. p. 155°, is obtained, closely resembling the mercurichloride-hydrochloride described above. This result favours the oxonium structure for the original dibromide. D. F. T.

Influence of Constitution on the Basic Property of Oxygen. I. BROJENDRA NATH GHOSH (T., 1915, **107**, 1588—1605).—The salt-forming power of an oxygen atom in various 6-membered ring systems has been studied in order to determine whether the basic function is influenced by the constitution of the molecule. For the purposes of comparison, the compounds have been tested with perchloric acid, and although special agents may combine with a given oxygen compound, it is regarded as having insignificant additive power if it forms no perchlorate. It is found that the power of bivalent oxygen to form salts is increased by the presence in the molecule of "negative" groups, such as the ethylene linking, naphthalene or benzene nuclei, carbonyl or thiocarbonyl groups.

Dioxan (ethylene ether), $C_4H_8O_2$, being saturated, forms no perchlorate or chloride.

Dihydrobenzdioxin, $C_6H_4\colon O_2\colon C_2H_4$, was prepared by boiling together catechol, ethylene dibromide, fused potassium carbonate, and a little copper bronze; b. p. 212—214°/757 mm., D_4^{20} 1·180. It gives a *dinitro*-compound, colourless needles, m. p. 133—134°; a *trinitro*-derivative, colourless needles, m. p. 155°; a *bromo*-derivative, b. p. 275—276°/754 mm.; and a *dibromo*-compound, colourless needles, m. p. 138°, but forms no salts.

1-Bromo-2-naphthol was heated in nitrobenzene with potassium carbonate and copper powder, and thus condensed to *di-αβ-naphthdioxin*, $C_{10}H_6{<}^{O}_{O}{>}C_{10}H_6$, which crystallises in pale yellow needles, m. p. 184—185°. This forms a green *ferrichloride* when ethereal solutions of the components are mixed; a *dipicrate*, chocolate-coloured needles, m. p. 156°; and a *diperchlorate*, $C_{20}H_{12}O_2,2HClO_4$, purple needles.

Diketodioxan (ethylene oxalate), $C_2H_4\colon O_2\colon C_2O_2$, forms a *dihydrochloride*, m. p. 152°, a *dihydrobromide*, m. p. 132° (decomp.), a *dipicrate*, yellow needles, m. p. 115°, and a *perchlorate*,

$$C_4H_4O_4,HClO_4.$$

Diketodihydrobenzdioxin, $C_6H_4\colon O_2\colon C_2O_2$, forms a *dipicrate*, m. p.

112°, a *disulphate*, m. p. 271° (decomp.), a *dihydrochloride*, m. p. 175°, and a *diperchlorate*.

Molecular quantities of 2 : 3-dichloro-α-naphthaquinone and pyrogallol were heated in pyridine solution, when *4-hydroxy-6 : 11-diketobenz-ββ-naphthdioxin*, $C_6H_4<\begin{matrix}CO\cdot C\cdot O\\ CO\cdot C\cdot O\end{matrix}>C_6H_3\cdot OH$, was obtained in purple needles, m. p. 288°. This gives an insoluble *sodium* salt, a green *ferrichloride*, an explosive, dark-coloured *diperchlorate*, a brown *dihydrochloride*, and an *acetyl* derivative, $C_{18}H_{10}O_6$, pale pink needles, m. p. 154°.

Catechol was condensed with ethyl chloroacetate in the presence of sodium ethoxide to *ethyl o-hydroxyphenoxyacetate*,

$$OH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2Et,$$

colourless needles, m. p. 48°, and this was condensed further, by boiling with concentrated hydrochloric acid, to *ketodihydrobenzdioxin*, $C_6H_4<\begin{matrix}O\cdot CO\\ O\cdot CH_2\end{matrix}$, colourless prisms, m. p. 135°. The latter compound forms a *dipicrate*, m. p. 125°, a *dihydrochloride*, m. p. 131°, a *dinitrate*, m. p. 113° (decomp.), and a *diperchlorate*, $C_8H_6O_3,2HClO_4,\frac{1}{2}H_2O$.

Benzdioxole (catechol methylene ether), dihydrodioxole (methylene ethylene ether), tetrahydropyran, and dihydrobenzpyran are not soluble in acids.

7-Hydroxy-2-methyl-4-methylene-γ-benzpyran,

$$OH\cdot C_6H_3<\begin{matrix}O\text{------}CMe\\ C(CH_2)\cdot CH\end{matrix},$$

forms a *hydrobromide*, with $\frac{1}{2}H_2O$, m. p. 217° (decomp.), a *perchlorate*, with $2H_2O$, an explosive, yellow powder, and a *platinichloride*, $2C_{11}H_{10}O_2,H_2PtCl_6,2H_2O$, glistening, yellow plates.

In addition to the known salts of coumarin, the following have been prepared: *picrate*, m. p. 112°, *sulphate*, m. p. 155—156°, and *perchlorate*, $C_9H_6O_2,HClO_4$, a very deliquescent powder.

2-Thio-1 : 2-benzpyran, $C_6H_4<\begin{matrix}O\text{---}CS\\ CH:CH\end{matrix}$, forms a *picrate*, m. p. 118°, a *hydrochloride*, pale yellow needles, m. p. 62°, and a *perchlorate*.

4-Methylcoumarin, $C_6H_4<\begin{matrix}O\text{---}CO\\ CMe:CH\end{matrix}$, yields a *picrate*, m. p. 65°, and a *perchlorate*. 4 : 6-Dimethylcoumarin forms a *picrate*, m. p. 124°, a *sulphate*, m. p. 168—169°, a *nitrate*, m. p. 175°, and a *perchlorate*. 6 : 7-Dimethylcoumarin gives a *picrate*, m. p. 124°, a *sulphate*, m. p. 135°, a *nitrate*, m. p. 140—141°, and a *perchlorate*. The latter coumarin was fused with phosphorus pentasulphide, and thus converted into *2-thio-6 : 7-dimethyl-1 : 2-benzpyran*,

$$C_6H_2Me_2<\begin{matrix}O\text{---}CS\\ CH:CH\end{matrix},$$

which crystallises in yellow needles, m. p. 159—160°, and forms the *oxime*, $C_{11}H_{11}O_2N$, m. p. 215°, and *phenylhydrazone*, m. p. 168°, of 6 : 7-dimethylcoumarin, when treated in the usual manner.

4 : 6 : 7-Trimethylcoumarin forms a *picrate*, m. p. 105°, a *nitrate*, m. p. 118° (decomp.), a *sulphate*, m. p. 92°, a *perchlorate*, and a *platinichloride*. This coumarin was also converted by fusion with phosphorus pentasulphide into *2-thio-4 : 6 : 7-trimethyl-1 : 2-benzpyran*, $C_6H_2Me_2<\begin{matrix}O-\!\!-CS\\ CMe{:}CH\end{matrix}$, golden-yellow needles, m. p. 158—159°, and from this, the *oxime*, very pale yellow needles, m. p. 179—180°, and *phenylhydrazone*, yellow needles, m. p. 147°, of 4 : 6 : 7-trimethylcoumarin were prepared.

7-Hydroxy-4-methylcoumarin, $OH{\cdot}C_6H_3<\begin{matrix}O-\!\!-CO\\ CMe{:}CH\end{matrix}$, yields a *mercurichloride*, a *picrate*, m. p. 108°, a *hydrochloride* (also obtained by passing hydrogen chloride into a solution of resorcinol and ethyl acetoacetate in glacial acetic acid), a *sulphate*, m. p. 175° (decomp.), and a *perchlorate*.

3-Acetylcoumarin, $C_6H_4<\begin{matrix}O-\!\!-CO\\ CH{:}CAc\end{matrix}$, forms a *semicarbazone*, m. p. 231°, a picrate, m. p. 75°, a *hydrochloride*, m. p. 108° (decomp.), and a *perchlorate*.

4-Methyl-1 : 2-α-naphthapyrone, $C_{10}H_6<\begin{matrix}O-\!\!-CO\\ CMe{:}CH\end{matrix}$, yields a *mercurichloride*, a *picrate*, m. p. 89°, a *hydrochloride*, m. p. 178° (decomp.), a *sulphate*, m. p. 62°, a *nitrate*, m. p. 78°, and a *perchlorate*. It was also converted by fusion with phosphorus pentasulphide into *2-thio-4-methyl-1 : 2-α-naphthapyrone*, $C_{14}H_{10}OS$, golden-yellow needles, m. p. 186°, and this forms a *mercurichloride*, a *picrate*, m. p. 167°, and a *perchlorate*. J. C. W.

The Chemical Constituents of the Bituminous Tar Oils rich in Sulphur (Ichthyol Oils). I. HELMUTH SCHEIBLER (*Ber.*, 1915, **48**, 1815—1826).—By the dry distillation of certain bituminous minerals there may be obtained tar oils, from which medicinal preparations containing combined sulphur, for example, ichthyol, are produced. The crude oils are treated with sulphuric acid, which renders them emulsifiable with water after neutralisation, probably due to a partial conversion into salts of 'sulpho'-acids. Little is known of the chemical nature of these oils.

The author has examined samples of the crude oil from the Tyrol, and from South France, the present results referring to the material of the latter origin. By distillation under reduced pressure the oil was separated into fractions, all of which were found to include certain constituents which could be removed by treatment with sodium with formation of dark-coloured, insoluble compounds. The sodium compounds when treated with water yielded oils which were insoluble in aqueous alkalis and showed a marked tendency to polymerisation; it is therefore probable that these compounds contain an acidic methylene radicle, such as is present in the *cyclo*-pentadienes, indene, and fluorene.

If the oil remaining after the sodium treatment is washed with dilute hydrochloric acid in order to remove basic constituents, the

residual oil is paler than the original, but the various fractions exhibit markedly similar chemical properties; a solution in light petroleum is turned brownish-red by sulphuric acid, the oil by itself being discoloured and reducing the sulphuric acid to sulphur dioxide; fuming nitric acid causes immediate inflammation; a mixture with phenanthraquinone in acetic acid solution gives a violet-red coloration on the addition of a drop of sulphuric acid, a reaction which is characteristic of certain of the alkylthiophens. The oils purified in this way still retain a small quantity of oxygen compounds, which can be removed by submitting them to treatment with a magnesium alkyl haloid, followed by sodium; it would thus appear that the oxygen constituents are of ketonic nature.

The final pale yellow products still contained a very considerable proportion of sulphur; thus the fraction b. p. 170—180°/360 mm., D^{20} 0·901, contained 14·3% of this element. Judged by its sulphur-content, this liquid must consist largely of propyl- or butyl-thiophen or of isomerides of these substances. By treatment in light petroleum with acetyl chloride and aluminium chloride under prescribed conditions, this fraction yielded a mixture of acetyl derivatives, b. p. 118—127°, containing 17·7% sulphur; this mixture yielded a semicarbazone, m. p. 178—192°, the composition, $C_{10}H_{15}ON_3S$, of which indicated it to be the semicarbazone of an acetylpropylthiophen or possibly of an isomeride or mixture of isomerides.

The halogen elements and the mercuric salts proved of less value than acetyl chloride for the separation of definite constituents of the oils. A sample of crude Tyrol oil gave a fraction, b. p. 130—140°, which yielded a *mercurichloride*, leaflets, m. p. 189—193° (compare Steinkopf and Bauermeister, A., 1913, i, 427).

The neutral constituents of the crude oil, which are removable by sodium, also contain combined sulphur, and the suggestion is made that these may be derived from condensed ring systems embodying the *cyclo*pentadiene and the thiophen nuclei.

D. F. T.

Sulphones of the Thiophen Series. O. HINSBERG (*Ber.*, 1915, **48**, 1611—1614).—When tetraphenylthiophen and 3:4-diphenylthiophen are warmed with glacial acetic acid and 30% hydrogen peroxide, they give yellow dioxides with high m. p.'s, which behave like sulphones, for they cannot easily be reduced. The sulphur in these compounds changes from bivalent to sexavalent, which is remarkable in view of the fact that thiophen derivatives are indifferent towards alkyl iodides.

Tetraphenylthiophen (thionessal) was dissolved in hot acetic acid and warmed with 30% hydrogen peroxide ($2\frac{1}{2}$—3 mols.) for some hours. *Tetraphenylthiophen dioxide*, $C_4Ph_4SO_2$, separated on cooling, in deep yellow prisms, m. p. 265°. 3:4-*Diphenylthiophen*, $C_4H_2Ph_2S$, was prepared by keeping 3:4-diphenylthiophendicarboxylic acid (A., 1910, i, 335) molten for a time, and was crystallised from chloroform or acetic acid, in prisms, m. p. 114°. The

dioxide, $C_{16}H_{12}O_2S$, formed pale yellow, slender needles, or prisms, m. p. 182°.

Lanfry (A., 1911, i, 740) obtained a dioxide, $C_4H_4O_2S$, from thiophen by the action of hydrogen peroxide. This differs from the above compounds in having a low m. p., below −25°, and being easily reduced by zinc and acetic acid, and it seems, therefore, not to be a sulphone. J. C. W.

Veratrine and some of its Derivatives. II. GEO. B. FRANKFORTER and W. KRITCHEVSKY (*J. Amer. Chem. Soc.*, 1915, **37**, 2567—2569).—Alkaloids in general appear to form sparingly soluble additive compounds when treated in carbon disulphide solution with chloral or bromal. The compounds were more closely examined in the case of veratrine (cevadine) and cevine.

By mixing a carbon disulphide solution of veratrine with suitable quantities of chloral, two additive compounds, respectively $2C_{32}H_{49}O_9N,CCl_3\cdot CHO$, m. p. 220°, and $2C_{32}H_{49}O_9N,3CCl_3\cdot CHO$, m. p. 209°, were obtained (compare Frankforter, A., 1896, i, 497). Cevine gave an additive compound, $C_{27}H_{43}O_8N,CCl_3\cdot CHO$, m. p. 206—208°. In a similar way, with bromal there were obtained from veratrine and cevine respectively the compounds

$$2C_{32}H_{49}O_9N,CBr_3\cdot CHO,$$

a bright yellow powder, m. p 162°, and $2C_{27}H_{43}O_8N,CBr_3\cdot CHO$, a bright yellow powder, m. p. 106°.

When dried at 130—140° for several hours the whole of the added chloral or bromal was expelled from these compounds. D. F. T.

A New Oxidation Method. II. The Action of Aldehydes on Hydramines of the Pyrrolidine and Piperidine Groups. K. HESS, F. MERCK, and CL. UIBRIG (*Ber.*, 1915, **48**, 1886—1906. Compare A., 1914, i, 199; 1913, i, 1378).—An extension of the discovery that secondary hydramines of the pyrrolidine group can be converted by the action of formaldehyde into tertiary aminoketones, an example already described being the conversion of the substance $C_4H_8N\cdot CH_2\cdot CHMe\cdot OH$ into $C_4H_7NMe\cdot CH_2\cdot COMe$. The reaction can be effected with other aldehydes, the products then being other 1-alkylpyrrolidyl ketones; primary alcohol derivatives can also be used in place of secondary alcohols, aldehydic compounds then being obtained.

β-2-Pyrrylethyl alcohol, $C_4H_4N\cdot CH_2\cdot CH_2\cdot OH$, prepared by the interaction of magnesium pyrryl bromide and ethylene oxide in ether–benzene solution, is a colourless oil, b. p. 102—104°/0·06 mm., which can be reduced in acetic acid solution by hydrogen and platinum-black with formation of *β-2-pyrrolidylethyl alcohol*, $C_4H_8N\cdot CH_2\cdot CH_2\cdot OH$, a basic, highly refractive, viscous oil, b. p. 78—80°/0·036 mm. This reacts with formaldehyde in alkaline solution at 110—124°, giving *β-1-methyl-2-pyrrolidylethyl alcohol*, $C_4H_7NMe\cdot CH_2\cdot CH_2\cdot OH$, a somewhat viscous liquid, b. p. 110—112°/14 mm., and in solution in hydrochloric acid, yielding a compound, probably *1-methyl-2-pyrrolidylacetaldehyde*,

$$C_4H_7NMe\cdot CH_2\cdot CHO,$$

a mobile, highly refractive oil, b. p. 79—80°/15—16 mm., of unpleasant, pungent odour; *picrate*, indistinct crystals. This difference between the action of formaldehyde in hydrochloric acid and in alkaline solutions seems to be a general one, as the following results show.

β-6-Picolyl-2-ethyl alcohol when reduced by sodium and alcohol or by hydrogen and platinum-black yields β-6-*methyl-2-piperidylethyl alcohol*, $CH_2{<}{\substack{CH_2{-}{-}CH_2\\ CHMe{\cdot}NH}}{>}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, in two geometrical isomerides, a less soluble α-form, polygonal tablets, m. p. 99°, and a more soluble β-form, b. p. 115—117°/22 mm. These two compounds were converted by formaldehyde in the presence of hydrochloric acid into two isomeric 1:6-*dimethylpiperidyl-2-acetaldehydes*, basic, mobile oils of narcotic odour, b. p. 84—85·5°/18 mm. and 85—87°/21 mm. respectively, *picrates*, prisms or tablets, m. p. 178°, and indistinct crystals, m. p. 135° respectively; the former base gave a mirror-like deposit of silver from silver nitrate solution, and with phenylhydrazine produced a *phenylhydrazone* which crystallised in needles; it was also reconverted by hydroxylamine in warm aqueous solution into the original methylpiperidylethyl alcohol.

β-2-Piperidylethyl alcohol reacted with formaldehyde in dilute hydrochloric acid solution at 120—125°, giving 1-*methyl-2-piperidylacetaldehyde*, $CH_2{<}{\substack{CH_2{-}CH_2\\ CH_2{\cdot}NMe}}{>}CH{\cdot}CH_2{\cdot}CHO$, a mobile oil of narcotic odour, with reducing properties; *picrate*, prisms, m. p. 154°.

α-Pyrrolidylethyl alcohol, $C_4H_8N{\cdot}CHMe{\cdot}OH$, is able to react in the general manner, not only with formaldehyde, but also with other aldehydes. The product with formaldehyde solution in the presence of hydrochloric acid at 120° is 1-*methylpyrrolidyl methyl ketone*, ${\substack{CH_2{\cdot}CHAc\\ \vert \\ CH_2{-}{-}CH_2}}{>}NMe$, an oil of the usual narcotic odour, b. p. 56—57°/26 mm.; *picrate*, m. p. 174—175°. Acetaldehyde under similar conditions gives rise to 1-*ethyl-2-pyrrolidyl ethyl ketone*, ${\substack{CH_2{\cdot}CHAc\\ \vert \\ CH_2{-}{-}CH_2}}{>}NEt$, b. p. 68—70°/17 mm., and benzaldehyde to 1-*benzyl-2-pyrrolidyl methyl ketone*, ${\substack{CH_2{\cdot}CHAc\\ \vert \\ CH_2{-}{-}CH_2}}{>}N{\cdot}CH_2Ph$, b. p. 139—141°/21 mm.; *picrate*, m. p. 163°.

2-Pyrryl propyl ketone (Oddo, A., 1910, i, 426) was reduced with sodium and alcohol to α-2-*pyrrolidylbutyl alcohol*,

$$\substack{CH_2{\cdot}CH_2\\ \vert \\ CH_2{-}NH}{>}CH{\cdot}CHPr{\cdot}OH,$$

needles, m. p. near 60°, b. p. 102—104°/19 mm. (*picrate*, prisms, m. p. 103°), which on treatment with formaldehyde solution in the presence of hydrochloric acid at 125—130° gave a substance, probably 1-*methyl-2-pyrrolidyl propyl ketone*,

$$\substack{CH_2{-}CH_2\\ \vert \\ CH_2{\cdot}NMe}{>}CH{\cdot}COPr,$$

a colourless oil, b. p. 83—85°/35 mm.; this reacts with hydroxylamine in aqueous solution, yielding the original pyrrolidylbutyl alcohol.

γ-2-Piperidyl*iso*propyl alcohol reacts with formaldehyde in aqueous solution containing hydrochloric acid at 115—128°, yielding 1-*methylpiperidyl-2-acetone*, $CH_2{<}\begin{array}{l}CH_2\text{—}CH_2\\CH_2\cdot NMe\end{array}{>}CH\cdot CH_2\cdot COMe$, a colourless, mobile oil, b. p. 82—84°/19 mm., 210°/738 mm. (*aurichloride*, prisms, m. p. 115—116°; *picrate*, yellow needles, m. p. 160—161°), which may be identical with *iso*methylpelletierine (Piccinini, A., 1899, i, 829).

The course of the above condensations with formaldehyde probably passes through the intermediate formation of a compound of the type of aldehyde–ammonia, for example, in the case of pyrrolidyl*iso*propyl alcohol the compound would have the structure $\begin{array}{l}CH_2\text{———}CH_2\\CH_2\cdot N(CH_2\cdot OH)\end{array}{>}CH\cdot CHEt\cdot OH$, in which the group attached to the nitrogen subsequently oxidises the neighbouring alcoholic group. Indeed, if formic acid is present, this substance undergoes oxidation more readily than the hydroxyl of the group attached at the 2-position of the molecule, and the action of formaldehyde in aqueous solution containing formic acid at 110—115° produces carbon dioxide and α-1-*methyl-2-pyrrolidylpropyl alcohol*,

$$\begin{array}{l}CH_2\text{—}CH_2\\CH_2\cdot NMe\end{array}{>}CH\cdot CHEt\cdot OH,$$

a liquid, b. p. 83°/14—15 mm.; *picrate*, needles, m. p. 153—154°.

Details are given of a method for the quantitative demethylation of scopoline with potassium permanganate solution, the product being pure norscopoline.

The action of hydroxylamine on many of the above ketonic derivatives in regenerating the original secondary or primary alcohol, as described above, is explained as a reversal of the process by which the ketonic compounds are produced, as represented by the typical example:

$$\begin{array}{l}CH_2\text{—}CH_2\\CH_2\cdot NMe\end{array}{>}CH\cdot COPr + H_2O \rightleftharpoons \begin{array}{l}CH_2\text{—}CH_2\\CH_2.NMe\end{array}{>}CH\cdot CPr(OH)_2 \rightleftharpoons$$

$$\begin{array}{l}CH_2\text{———}CH_2\\CH_2\cdot N(CH_2.OH)\end{array}{>}CH\cdot CHPr\cdot OH \rightleftharpoons$$

$$\begin{array}{l}CH_2\cdot CH_2\\CH_2\text{—}NH\end{array}{>}CH\cdot CHPr\cdot OH + CH_2O.$$

Indeed, it is possible to detect the presence of formaldehyde in the solution which has been treated with hydroxylamine.

D. F. T.

The Halogen Pyrroles. II. K. HESS and F. WISSING (*Ber.*, 1915, **48**, 1884—1886. Compare A., 1914, i, 725).—By the action of chlorine on magnesium pyrryl bromide prepared from pyrrole and magnesium ethyl bromide, the authors have produced a chloropyrrole (*loc. cit.*). In a similar manner by the addition of a cooled ethereal solution of bromine to an ethereal solution of

magnesium pyrryl bromide, followed by successive treatment with ice-cold water, distillation of the ether, and distillation of the aqueous residue under reduced pressure, the authors have obtained an oil which solidifies to colourless crystals; these doubtless consist of *bromopyrrole*, but the substance is exceedingly unstable, and decomposes in a few minutes, when dry, with a feeble explosion.

If the aqueous residue obtained in the course of the above method of preparation is distilled with steam under ordinary pressure, a highly refractive oil, probably a decomposition product of the above bromopyrrole, is obtained, the composition of which indicates it to be a *bromodipyrrole*, $C_8H_7N_2Br$.

With iodine it was not found possible to isolate any reaction product, decomposition setting in immediately. D. F. T.

The Alkylation of Pyrroles. III. K. HESS, F. WISSING, and A. SUCHIER (*Ber.*, 1915, **48**, 1865—1884. Compare A., 1914, i, 725).—In an attempt to prepare phyllopyrrole by the interaction of ethyl bromide and magnesium 2:3:5-trimethylpyrryl bromide, the authors have obtained the isomeric compound with the ethyl group attached at the nitrogen atom, together with basic products, the chief of which is proved to be 2:3:5-trimethyl-3-ethylpyrrolenine.

The 2:3:5-trimethylpyrrole was prepared by a modification of the method of Fischer and Bartholomäus (A., 1912, i, 297). The most favourable conditions were investigated for the formation of the pyrrolenine product, the chief factors being the temperature and the duration of the action of the ethyl bromide on the magnesium compound; the mixture of the reagents with ether was therefore kept at the b. p. of the solvent for fifty hours. The reaction product, from which unaltered trimethylpyrrole was removed by coupling with diazobenzenesulphonic acid, was distilled, the fraction, b. p. 53—54°/22 mm., consisting of 2:3:5-*trimethyl*-3-*ethylpyrrolenine*, $\begin{array}{l}CH{=\!=\!=}CMe\\ CMeEt{-}CMe\end{array}\!\!>\!N$, b. p. 158—159°/742 mm.; *picrate*, needles, m. p. 188—190° (decomp.); *mercurichloride*, colourless needles, m. p. 122°; *platinichloride*, orange-red crystals, m. p. 195° (decomp.); the m. p., 65—66°, of the crystalline *aurichloride* proved the distinct nature of this base from a somewhat similar product of Ciamician and Anderlini (A., 1889, 58). That the base is not a pyridine derivative was proved by oxidation with potassium permanganate giving only oxalic acid, but the final demonstration of its identity was made by an independent synthesis. 2:5-Dimethyl-3-ethylpyrrole, a colourless oil, b. p. 112°/42 mm. (*picrate*, yellowish-red and amorphous; *mercurichloride*, amorphous), obtained by heating ethyl 2:5-dimethyl-3-ethylpyrrole-4-carboxylate with sulphuric acid, when converted into the corresponding magnesium pyrryl iodide derivative and treated with an ethereal solution of methyl iodide, gives as reaction product a mixture of phyllopyrrole and the above 2:3:5-trimethyl-3-ethylpyrrolenine.

The second fraction from the distillation of the product from the interaction of magnesium 2:3:5-trimethylpyrryl bromide and ethyl bromide had b. p. 85—87°/22 mm. and contained a substance of

the composition $C_{10}H_{17}N$, identical with the product previously described as $C_8H_{13}N$ (Hess and Wissing, A., 1914, i, 725); *picrate*, golden-yellow, microscopic prisms, m. p. 140—141°. The third fraction, b. p. 114—115°/26 mm., contained a substance isomeric with phyllopyrrole, probably 2:3:5-*trimethyl*-1-*ethylpyrrole*; *mercurichloride*, crystalline.

An extension of the above reaction was made to magnesium 2:3-dimethyl-5-ethylpyrryl bromide, which on treatment with an ethereal solution of ethyl bromide gave 2:3-*dimethyl*-3:5-*diethyl pyrrolenine*, b. p. 70—73°/26 mm., 173°/726 mm.; *picrate*, yellow, m. p. 190°; *mercurichloride*, needles, m. p. 115°; *platinichloride*, orange-coloured granules, m. p. 169° (decomp.); *aurichloride*, granules, m. p. 97—98°, or tablets with $\frac{1}{2}$EtOH, m. p. 215° (decomp.).

The authors maintain the correctness of the statement (Hess and Wissing, *loc. cit.*) that the ethylation of pyrrole by the action of ethyl bromide on magnesium pyrryl bromide is 2-ethylpyrrole, and not 3-ethylpyrrole, as stated by Oddo and Mameli (A., 1914, i, 80, 1142). D. F. T.

The Constitution of the Nitropyrrole-2-carboxylic Acids. WILLIAM J. HALE and WILLIAM V. HOYT (*J. Amer. Chem. Soc.*, 1915, **37**, 2538—2552).—Three nitropyrrole-2-carboxylic acids are known, the first, m. p. 146°, having been obtained by Ciamician and Danesi (A., 1882, 875) from pyrocoll by nitrating and hydrolysing the resulting dinitropyrocoll. By the nitration of methyl pyrrole-2-carboxylate, Anderlini (A., 1890, 66) was able to obtain two other nitropyrrole-2-carboxylic acids, m. p. 217° and 161° respectively. The present investigation deals with the positions of the nitro-group in these three isomerides.

By the action of sodium nitromalonaldehyde, $NO_2Na{:}C(CHO)_2$, on glycine ethyl ester hydrochloride in alcoholic solution, *ethyl β-nitro-β-aldehydoethylideneaminoacetate*,

$$CHO{\cdot}CH(NO_2){\cdot}CH{:}N{\cdot}CH_2{\cdot}CO_2Et,$$

is obtained as pale yellow prisms, m. p. 104° (*phenylhydrazone*, crystalline), which in alcoholic solution under the influence of a little sodium hydroxide readily undergoes further condensation to *ethyl 4-nitropyrrole-2-carboxylate*, $\begin{matrix}C(NO_2){=}CH\\ CH{:}C(CO_2Et)\end{matrix}\!\!>\!NH$, almost colourless prisms, m. p. 174°. The analogous methyl ester, almost colourless prisms, m. p. 198°, can be prepared in a similar manner (compare Anderlini, *loc. cit.*). Hydrolysis of the ethyl ester yielded 4-nitropyrrole-2-carboxylic acid, m. p. 217°, identical with Anderlini's product, of which the constitution is thus proved.

The constitution of the remaining nitropyrrole-2-carboxylic acids should be capable of decision by the fact that the 3-nitropyrrole-2-carboxylic acid should, on elimination of carbon dioxide, yield the same nitropyrrole as the above 4-nitropyrrole-2-carboxylic acid. The only nitropyrrole known was prepared by Angeli and Allessandri (A., 1911, i, 397), who on rather slight evidence described it as 4-nitropyrrole. Their decision, however, is justified by the

action of heat on 4-nitropyrrole-2-carboxylic acid when mixed with naphthalene, which effects the formation of a nitropyrrole identical with that obtained by these investigators, who, however, overlooked the fact that the simple nitropyrrole, m. p. 63·5°, readily polymerises to a 4:4′-*dinitrodipyrrole*, yellow prisms or platelets, m. p. 101°, for which the constitution

$$CH\Big\langle\begin{array}{l}C(NO_2)\cdot CH\cdot CH\cdot C(NO_2)\\ NH\text{——}CH\cdot CH\text{——}NH\end{array}\Big\rangle CH$$

is suggested; in aqueous solution an equilibrium mixture of the two forms is apparently produced.

When the nitropyrrole-2-carboxylic acid, m. p. 146°, was heated with naphthalene under pressure in a similar way, the same mixture of 4-nitropyrrole, m. p. 63·5°, and 4:4′-dinitrodipyrrole, m. p. 101°, was obtained, so that this acid must be 3-nitropyrrole-2-carboxylic acid. The third acid, m. p. 161°, which the authors found to be obtained most conveniently from the residues obtained in the nitration of pyrocoll, decomposes only slowly when heated with naphthalene, and only a small amount of an unstable, yellow oil was obtained; this oil is probably 2-nitropyrrole, the instability of which is to be expected by analogy to the α-nitro-derivatives of thiophen and furan. D. F. T.

Action of Alkalis on the Nitrosoamines of 4-Piperidone Derivatives. ERIC DODDRELL EVENS, EDGAR CRANTHORNE GIFFORD, and WALTER EDWARD LAMBOURNE GRIFFITHS (T., 1915, **107**, 1673—1677).—Francis has shown (T., 1912, **101**, 2358) that nitrosotriacetonamine is quantitatively converted into phorone, water, and nitrogen in the presence of a small quantity of an alkali. This catalytic action of hydroxyl ions has been further investigated in the case of other nitrosoamines (Francis, Geake, and Roche, T., 1915, **107**, 1651), and the present paper deals with some of the materials used in that study.

The oxalates of the substituted diacetonamines separate when diacetonamine oxalate is condensed with aldehydes in alcoholic solutions. The yields obtained by the authors were: *iso*butyl-, 80%; phenyl-, 62%; cinnamyl-, 60%; *iso*valeryl-, 60%; vinyl-, 60%; anisyl-, 50%; p-*tolyldiacetonamine oxalate*, 50%; n-*butyldiacetonamine oxalate*, 42%; heptyl-, 40%; and n-*propyldiacetonamine oxalate*, 26%, which indicates the relative reactivity of the aldehydes.

The oxalates were converted into the nitrosoamines by means of sodium nitrite. The following nitrosoamines appear to be new: *nitrosopropyldiacetonamine*, $C_9H_{16}O_2N_2$, m. p. 28°; *nitroso*-n-*butyldiacetonamine*, $C_{10}H_{18}O_2N_2$, m. p. 44°; *nitroso*-p-*tolyldiacetonamine*, $C_{14}H_{18}O_2N_2$, an oil; *nitrosocinnamyldiacetonamine*, $C_{15}H_{18}O_2N_2$, m. p. 126°; *nitrosovaleryldiacetonamine*, $C_{11}H_{20}O_2N_2$, m. p. 59°; *nitrosoheptyldiacetonamine*, $C_{13}H_{24}O_2N_2$, an oil; and *nitrosoanisyldiacetonamine*, $C_{14}H_{18}O_3N_2$, m. p. 74°.

Few of these nitrosoamines gave analogues of phorone as readily as nitrosotriacetonamine. Thus nitrosophenyldiacetonamine, m. p.

75° (Kohn and Wenzel, A., 1907, i, 237), when warmed with alcohol containing a little sodium ethoxide, gave *α-phenyl-ε-methyl-$\Delta^{\alpha\delta}$ hexadien-γ-one*, $CMe_2:CH\cdot CO\cdot CH:CHPh$, as a yellow oil which spontaneously changed to the white *dimeride*, m. p. 88°. Nitrosoanisyldiacetonamine gave a quantitative yield of *α-p-methoxyphenyl-ε-methyl-$\Delta^{\alpha\delta}$-hexadien-γ-one*,

$$CMe_2:CH\cdot CO\cdot CH:CH\cdot C_6H_4\cdot OMe,$$

large, yellow plates, m. p. 56°. Nitrosocinnamyldiacetonamine readily gave *α-phenyl-η-methyl-$\Delta^{\alpha\gamma\zeta}$-octatrien-ε-one*,

$$CMe_2:CH\cdot CO\cdot CH:CH\cdot CH:CHPh,$$

which crystallised in yellow needles or plates, m. p. 87·5°, and formed a *hexabromide*, m. p. 160°. Nitroso*iso*butyldiacetonamine, m. p. 56° (*ibid.*), yielded a small amount of *βη-dimethyl-$\Delta^{\gamma\zeta}$-octadien-ε-one*, $CMe_2:CH\cdot CO\cdot CH:CH\cdot CHMe_2$, b. p. 93—98°/11 mm., D^{25} 0·8804, α_D^{25} 1·48056, the *tetrabromide* of which had m. p. 76—77°.

The other nitrosoamines gave oils with pleasant odours, like phorone, but they could not be purified. J. C. W.

Transformation of Maleic Acid into Succinic Derivatives with the Help of Pyridine Bases. O. E. LUTZ (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1549—1561. Compare A., 1910, i, 879).—Maleic acid gives well-characterised acid salts with α- and β-picolines and with commercial lutidine and collidine. In alcohols and, to some extent, in other solvents these salts undergo isomeric change into anhydropicoliniumsuccinic and similar acids, which may also be obtained by the action of the above bases on *dl*-bromosuccinic acid; if the latter is replaced by *l*-bromosuccinic acid, the optically active anhydropicoliniumsuccinic acids are obtained. In the case of the acid β-picoline salt of maleic acid, heating at the melting point suffices to cause the above transformation. Similar changes accompany the action of pyridine on fumaric or itaconic acid, but they are not observed with citraconic or mesaconic acid.

α-Picoline Hydrogen maleate, $C_5NH_4Me,C_4H_4O_4$, has m. p. 76—77°.

dl-*Anhydro-α-picoliniumsuccinic acid*, $\begin{matrix} CH(CO_2H)\cdot C_5NH_4Me \\ CH_2 \text{———————} CO \end{matrix}\!\!>\!O$,

has m. p. 175—176° (decomp.), and the optically *active* compound obtained from *l*-bromosuccinic acid, m. p. 178—179° (decomp.), $[\alpha]_D$ +19·6° in dilute hydrochloric acid.

β-Picoline hydrogen maleate, $C_5H_4NMe,C_4H_4O_4$, melts below 80°, but the liquid solidifies immediately to dl-*anhydro-β-picoliniumsuccinic acid*, $C_{10}H_{11}O_4N$, m. p. 178·5—179·5° (decomp.). d-*Anhydro-β-picoliniumsuccinic acid*, obtained from β-picoline and *l*-bromosuccinic acid, has m. p. 175—177° and $[\alpha]_D$ +4·8° in dilute hydrochloric acid.

dl-*Anhydrolutidiniumsuccinic acid*, $\begin{matrix} CH(CO_2H)\cdot C_5NH_3Me_2 \\ CH_2 \text{———————} CO \end{matrix}\!\!>\!O$,

prepared from commercial lutidine, b. p. 154—158°, has m. p. 170—172° (decomp.), and the d-*isomeride*, obtained from *l*-bromo-

succinic acid and lutidine, has m. p. 168—170° (decomp.) and $[\alpha]_D$ +3·8° in dilute hydrochloric acid.

Collidine hydrogen maleate, $C_8H_{11}N,C_4H_4O_4$, prepared from commercial collidine, b. p. 168—170°, has m. p. 103—104°, and in presence of methyl or ethyl alcohol gradually undergoes conversion into dl-*anhydrocollidiniumsuccinic acid*, $\begin{array}{l}CH(CO_2H)\cdot C_8H_{11}N \\ CH_2 \text{———————} CO\end{array}\!\!>O$ which decomposes at 172—173°; d-*anhydrocollidiniumsuccinic acid*, prepared from collidine and *l*-bromosuccinic acid, has m. p. 168—169° (decomp.) and $[\alpha]_D$ +4·2° in dilute hydrochloric acid.

T. H. P.

Synthesis of 1-Methylpiperidine-2:6-dicarboxylic Acid. K. HESS and F. WISSING (*Ber.*, 1915, **48**, 1907—1912).—In the course of an investigation of the degradation products of scopoline, the authors have obtained a tertiary dicarboxylic acid derivative of piperidine which proves to be identical with 1-methylpiperidine-2:6-dicarboxylic acid, of which a method of synthesis is now described.

Synthetic lutidine, b. p. 142—144°/733 mm., was oxidised with potassium permanganate to lutidinic acid, and the product subsequently reduced with colloidal platinum and hydrogen by the Paal-Skita method to hexahydro-2:6-lutidinic acid; reduction in aqueous solution with sodium amalgam gave a product which yielded a mixture of two hydrochlorides, prismatic needles, and hexagonal tablets, $C_7H_{12}O_4NCl$, probably derived from geometrically isomeric acids. The hexahydro-acid, in the form of its hydrochdoride, was heated with formaldehyde solution at 135—140° for four hours, whereby the desired 1-*methylpiperidine*-2:6-*dicarboxylic acid*, hexagonal tablets, m. p. 225° (decomp.), was obtained in almost quantitative yield; *hydrochloride*, polygonal tablets, m. p. 225—226° (decomp.); *copper* salt, long needles, decomp. near 235°.

When piperidine is heated with formaldehyde solution at 110—115° for four hours, almost equal quantities of methylpiperidine and methylenepiperidine are obtained.

D. F. T.

Aromatic-Aliphatic Indigoid Dyes. W. HERZOG and AD. JOLLES (*Ber.*, 1915, **48**, 1574—1578).—Friedländer has shown that the anilides of *o*-diketones condense readily with compounds containing the group $\cdot CO\cdot CH_2\cdot$ to form indigoid dyes, and has prepared a large number of bi-aromatic, aromatic-cyclic aliphatic, and bi-cyclic aliphatic dyes by such means. Aromatic-aliphatic indigoid dyes have not been known hitherto, however, but some are now described. It is found that such a simple open-chain compound as methyl ethyl ketone does not contain a sufficiently reactive $\cdot CO\cdot CH_2\cdot$ group, but the β-diketones condense quite readily. The new dyes contain the characteristic chromophoric group, $\cdot CO\cdot C\colon C\cdot CO\cdot$, of a vat dye, but although they behave as vat dyes they have no affinity for vegetable or animal fibres. They are more soluble and more fusible than the purely aromatic indigotins.

Acetylacetone (pentan-$\beta\delta$-dione) was condensed with thionaphthenquinone–anilide in hot acetic anhydride, and the product, "*2-thionaphthen-3-pentanoneindigotin*" [*2-$\beta\delta$-diketo-γ-pentylidenethionaphthen*] $C_6H_4<\substack{CO\\S}>C:C(COMe)_2$, separated on cooling in long, reddish-yellow, silky needles, m. p. 142—143°. A 0·2% solution in chloroform is deep red, and the absorption band begins at 583 $\mu\mu$ and is complete after 571·5 $\mu\mu$. Acetonylacetone was also condensed with α-isatinanilide to form "*2-indole-3-pentanoneindigotin*" [*2-$\beta\delta$-diketo-γ-pentylideneindole*],

$$C_6H_4<\substack{CO\\NH}>C:C(COMe)_2,$$

which crystallises in vermillion needles, m. p. 200° (decomp.), and exhibits partial absorption after 540 $\mu\mu$ and total after 528 $\mu\mu$ in a 0·2% solution in chloroform. Equimolecular quantities of benzoylacetone and α-isatinanilide were also condensed, with the formation of "*2-indole-3-benzoylpropaneindigotin*" [*2-α-benzoylacetonylideneindole*], $C_6H_4<\substack{CO\\NH}>C:CBz\cdot COMe$, which crystallises in fiery-red needles, m. p. 180—181°. J. C. W.

2-Phenylquinoline-4-carboxylic Acid (Atophan) and its Oxidation Products. RUDOLF BOEHM and KONRAD BOURNOT (*Ber.*, 1915, **48**, 1570—1574).—In view of the interest in the fate of atophan in the human body, the authors have studied the effect on it of boiling alkaline permanganate, and have found that it suffers oxidation in two directions under the same conditions. In one reaction the pyridine ring is oxidised, and the chief product is 2-phenyl-4 : 5-benzoxazole, whilst in the other the benzene nucleus is attacked, and the main product is the new 2-phenylpyridine-4 : 5 : 6-tricarboxylic acid.

Pure 2-phenylquinoline-4-carboxylic acid has m. p. 212—213°, and is soluble in 20 parts of alcohol, 25 of methyl alcohol, 35 of acetone, and 250 of benzene at the boiling points of these solvents. The alkali salts are crystalline, and the sodium salt is only sparingly soluble in 15% sodium hydroxide.

For the oxidation, the pure acid was boiled with alkaline permanganate, and the 2-phenylbenzoxazole (benzenylaminophenol), $C_6H_4<\substack{O\\N}\geqslant CPh$, was removed as it was formed in a current of steam. The remainder was then filtered, rendered slightly acid by sulphuric acid, and evaporated until potassium sulphate crystallised out. The mother liquor from this was finally mixed with dilute sulphuric acid as long as a precipitate was formed. This consisted of an acid salt of the phenylpyridinetricarboxylic acid, from which the free acid was obtained by the action of hydrochloric acid. From 20 grams of atophan, 2 grams of 2-phenylbenzoxazole and 13 grams of the tricarboxylic acid were obtained.

2-Phenylpyridine-4 : 5 : 6-tricarboxylic acid, $C_{14}H_9O_6N$, crystallises in stout prisms with $1H_2O$ from water in airtight vessels, or in a felted mass of slender needles if the solution is allowed to evaporate,

and decomposes at 183—185°. The normal potassium, sodium, calcium, and cadmium salts are soluble, and the barium and *silver*, $C_{14}H_6O_6NAg_3,H_2O$, salts are almost insoluble. An *acid potassium* salt of the formula $C_{14}H_9O_6N + C_{14}H_8O_6NK + 3\frac{1}{2}H_2O$ crystallises in large, very thin tablets. When boiled with acetic acid and acetic anhydride, the tricarboxylic acid changes into 2-*phenylpyridine*-4:5-*dicarboxylic acid*, $C_{13}H_9O_4N$, which separates on cooling in pale yellow, silky needles or prisms, m. p. 248—250°. The alkali and barium salts are soluble, the *silver* salt is sparingly soluble, and an *acid potassium* salt, $C_{13}H_9O_4N,C_{13}H_8O_4NK$, crystallises readily in tufts of needles, decomp. 279°. The *dimethyl* ester forms colourless plates, m. p. 74°. J. C. W.

Conversion of Hydroacridine into Acridine. J. Boes (*Chem. Zentr.*, 1915, ii, 711; from *Apoth. Zeit.*, 1915, **30**, 406—407).—Acridine is obtained in 75% yield by heating hydroacridine for several hours at 100° with 78% sulphuric acid, fractionally precipitating the resin from the aqueous solution of the reaction product by the addition of ammonia, and finally precipitating the base by further addition of ammonia. G. F. M.

Spirans. VIII. A New Kind of Rearrangement with Oximes of Certain Ketones. Hermann Leuchs and Hubert Rauch (*Ber.*, 1915, **48**, 1531—1540).—When the oxime of 2-*o*-carboxybenzylhydrindone, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CH_2}{C(:NOH)}}{>}CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$, is heated with acetyl chloride in a sealed tube at 95° there is obtained ammonium chloride and dihydro*iso*coumarinhydrindonespiran, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CH_2}{CO{\cdot}O}}{>}C{<}{\genfrac{}{}{0pt}{}{CH_2}{CO}}{>}C_6H_4$, whilst if the same reagents are allowed to react at the ordinary temperature there is formed an intermediate product, the *hydrochloride* of the corresponding imino-compound, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CH_2}{CO{\cdot}O}}{>}C{<}{\genfrac{}{}{0pt}{}{CH_2}{C(:NH,HCl)}}{>}C_6H_4$, greenish-yellow crystals, m. p. 223° (decomp.), which on successive treatment with water and sodium carbonate solution undergoes conversion into the above ketonic spiran compound. In this case, therefore, the action of acetyl chloride appears to have induced an interchange of positions between a hydrogen atom and a hydroxyl or acetoxyl radicle, thus giving rise to a compound which passes easily into the lactone. Phosphorus pentachloride effects the normal Beckmann rearrangement, the solution of the carboxybenzylhydrindoneoxime in ether with this agent yielding a substance, $C_{17}H_{15}O_3N$, probably 3-*o*-carboxybenzyldihydrocarbostyril, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CH_2}{CO{\cdot}NH}}{>}CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$, needles, m. p. 235° (decomp.), together with the corresponding lactone, 1-*hydrindone-dihydrocarbostyril*-2:3-*spiran*, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CH_2}{CO}}{>}C{<}{\genfrac{}{}{0pt}{}{CH_2{\cdot}C_6H_4}{CO{-}NH}}$ tetragonal leaflets, m. p. 268°. The latter product predominated, but could be converted into the former by heating with diluted

sulphuric acid, the reverse change occurring at the m. p. of the carboxybenzyl compound.

In an analogous manner the action of acetyl chloride on 2-benzylhydrindoneoxime (needles, m. p. 122—123°, to a turbid liquid which becomes clear at 131°) caused the formation of *2-benzylidenehydrindonimine hydrochloride*, $C_6H_4<\genfrac{}{}{0pt}{}{CH_2}{C(:NH,HCl)}>C:CHPh$, yellow prisms, which when warmed with water or dilute hydrochloric acid is converted into 2-benzylidenehydrindone.

The above results, obtained by the action of acetyl chloride on the oximes of certain hydrindone compounds, supply another case of an oxidising effect produced by hydroxylamine.

The compound obtained earlier by the rearrangement of the monoxime of bishydrindonespiran under the influence of phosphorus pentachloride (Leuchs and Wutke, A., 1913, i, 973) can, in the light of the results now obtained with the oximes mentioned above, be definitely regarded as 1-hydrindonedihydro*iso*carbostyril-2 : 3-spiran. D. F. T.

Reductions with a Solution of Sulphur in Alkali Sulphide. A. COBENZL (*Chem. Zeit.*, 1915, **39**, 859—860).—The sulphonic acids of azo-dyes can be readily reduced by boiling with a solution of sulphur in aqueous alkali sulphide under atmospheric or increased pressure, with the production of a good yield of the corresponding diamine. Thus a 90% yield of phenyl-*p*-phenylenediamine was obtained from diphenylaminoazobenzenesulphonic acid (orange IV) by this treatment. The base on fusion with oxalic acid gave a dye which after sulphonation formed deep blue crystals, and by the Skraup reaction it was converted into 4-anilinoquinoline. The sulphonation, acetylation, and nitration of the base are described in detail. The preparation of phenylmethyl-*p*-phenylenediamine, naphthylene-1 : 4-diamine, dimethylnaphthylene-1 : 4-diamine, phenylnaphthylene-1 : 4-diamine, and α-naphthylnaphthylene-1 : 4-diamine by the reduction of the corresponding azo-compound obtained by coupling the monamine with diazotised sulphanilic acid, is described. So, for example, α-naphthylamine was coupled with diazotised sulphanilic acid, and the ammonium salt of the resulting α-naphthylamineazobenzene sulphonic acid was boiled for three hours with the sodium polysulphide solution, and naphthylene-1 : 4-diamine isolated as its hydrochloride. *p*-Anisidine and *m*-phenetidine were likewise prepared from the corresponding nitrophenol ethers by the sulphide reduction method in dilute alcoholic solution. G. F. M.

Diaminofluorenes. HERMANN EMDE (*Chem. Zentr.*, 1915, ii, 277—278; from *Apoth. Zeit.*, 1915, **30**, 293—295).—3 : 3′-Dinitrobenzidine, obtained by the hydrolysis of dinitrodiacetylbenzidine with aqueous methyl-alcoholic potassium hydroxide, can be converted satisfactorily by successive diazotisation and treatment with alcohol into 3 : 3′-dinitrodiphenyl. This compound, on reduction with stannous chloride in acetic acid solution, is converted into

3 : 3′-*diaminodiphenyl*, prisms or needles, m. p. 93·5°; *dihydrochloride*, crystals, decomp. near 300°; *sulphate*, more soluble in water than is benzidine sulphate; *nitrate*, pale brown needles, which carbonise above 200°; the Schiff's base, obtained by condensation with formaldehyde, was of variable nature, and attempts to convert it into 3 : 6-diaminofluorene, which was the aim of the investigation, failed.

In the direct nitration of fluorene to dinitrofluorene, the main product is always the 2 : 7-compound; reduction of the crude product with zinc dust and acetic acid yielded a mixture of bases, from which 2 : 7-*diaminofluorene*, prisms, m. p. 162° (*acetate*, decomp. at 274°), a base, possibly 2 : 6 : 7-triaminofluorene, m. p. 198°, and a new *diaminofluorene*, colourless needles (*dihydrochloride*, easily hydrolysed by water; *acetate*, decomp. at 269°), were separated by fractional crystallisation from benzene. D. F. T.

New Pyridazinones (Ketotetrahydropyridazines). LODOVICO MUNGIOLO (*Gazzetta*, 1915, **45**, ii, 299—304).—It has been shown by Fischer (*Annalen*, 1886, **236**, 147) and by Fittig (A., 1898, i, 196) that, when heated, hydrazones of γ-keto-acids yield pyridazinones. From arylhydrazones of lævulic and β-benzoylpropionic acids the author has prepared a number of these compounds.

Lævulic acid o-*tolylhydrazone* forms colourless prisms, m. p. 117°, and rapidly decomposes in the air. At 160—170° it undergoes a violent reaction, yielding 1-o-*tolyl*-3-*methylpyridazinone*,

$$CO<\begin{matrix}N(C_6H_4Me)\cdot N\\CH_2\text{———}CH_2\end{matrix}>CMe,$$

which forms colourless prisms, m. p. 65°, b. p. 330—340° (decomp.).

Lævulic acid p-*tolylhydrazone* forms colourless prisms, m. p. 93—95°, and 1-p-*tolyl*-3-*methylpyridazinone*, $C_{12}H_{14}ON_2$, slender plates, m. p. 59°.

1-as-m-*Xylyl*-3-*methylpyridazinone*, $C_{13}H_{16}ON_2$, forms tabular prisms, m. p. 81°, and decomposes violently at 160—170°.

1-s-ψ-*Cumyl*-3-*methylpyridazinone*, $C_{14}H_{18}ON_2$, forms needles, m. p. 72° (impure), and decomposes violently at 160—170°.

β-Benzylpropionic acid *o*-, *m*-, and *p*-tolylhydrazones and *as*-*m*-xylylhydrazone were obtained as oils, remaining liquid at the ordinary temperature.

3-*Phenyl*-1-o-*tolylpyridazinone*, $C_{17}H_{16}ON_2$, forms white, prismatic needles, m. p. 118°; 3-*phenyl*-1-m-*tolylpyridazinone*, shining, straw-like chips, m. p. 84°; 3-*phenyl*-1-p-*tolylpyridazinone*, white, prismatic needles, m. p. 119°; 3-*phenyl*-1-as-m-*xylylpyridazinone*, $C_{18}H_{18}ON_2$, colourless prisms, m. p. 138°; and 3-*phenyl*-1-s-ψ-*cumylpyridazinone*, $C_{19}H_{20}ON_2$, prismatic needles, m. p. 130°. T. H. P.

Pyrimidines. LXXVII. The Alkylation of 2-Thiolpyrimidines. TREAT B. JOHNSON and ROBERT C. MORAN (*J. Amer. Chem. Soc.*, 1915, **37**, 2591—2597).—Johnson and Haggard (A., 1915, i, 88) have observed that the sodium salt of 2-allylthiol-4-methyldihydropyrimid-6-one exhibits exceptional behaviour towards alkyl haloids, and this being probably due to the influence of the allyl

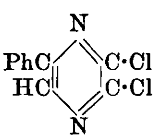
radicle, the authors have investigated the effect of substituting the still more negative benzoyl radicle in place of the vinyl group.

2-Benzoylmethylthiol-4-methyl-1 : 6-dihydropyrimid-6-one (Johnson and Moran, A., 1912, i, 913) does, in fact, react with bromoacetophenone in the same way as the allyl analogue, producing 6-benzoylmethoxy-2-benzoylmethylthiol - 4 - methylpyrimidine. The sodium salt also reacts with methyl iodide in alcoholic solution, giving 2-*benzoylmethylthiol*-1 : 4-*dimethyl*-1 : 6-*dihydropyrimid*-6-*one*, $CH{<}{\overset{CO\cdot NMe}{\underset{CMe—N}{}}}{>}CS\cdot CH_2Bz$, prisms, m. p. 155°, which on hydrolysis with hydrochloric acid gives 2 : 5-diphenyl-1 : 4-dithiene and 1 : 4-dimethyluracil. With ethyl bromide, reaction occurred with the exclusive formation of 6-*ethoxy*-2-*benzoylmethylthiol*-4-*methylpyrimidine*, $CH{<}{\overset{C(OEt):N}{\underset{CMe—N}{}}}{>}CS\cdot CH_2Bz$, flat prisms, with $\frac{1}{2}$AcOEt, m. p. 83·5°, or prisms, m. p. 86—88°, from light petroleum, which on hydrolysis gave 2 : 5-diphenyl-1 : 4-dithiene and 4-methyluracil. Abnormal results were obtained with benzyl chloride, a mixture of which with the sodium salt of 2-benzoylmethylthiol-4-methyl-1 : 6-dihydropyrimid-6-one in ethyl-alcoholic solution yielded 6-ethoxy-2-benzoylmethylthiol-4-methylpyrimidine, whilst the product in methyl-alcoholic solution was the corresponding 6-*methoxy*-2-*benzoylmethylthiolmethylpyrimidine*,

$$CH{<}{\overset{C(OMe):N}{\underset{CMe—N}{}}}{>}CS\cdot CH_2Bz,$$

slender needles, m. p. 143—144°, which on hydrolysis with hydrochloric acid gave 2 : 5-diphenyl-1 : 4-dithiene and 4-methyluracil. The possible mechanism of the formation of these abnormal products is discussed, the suggestion being made that the benzyl compound is actually first produced, but that successive addition of a molecule of the solvent alcohol and elimination of a molecule of benzyl alcohol occur with the production of the isolated alkyloxy-derivatives. D. F. T.

A Synthesis of 1 : 4-Diazines [Pyrazines] and of New Derivatives of Chloral and Bromal. ST. MINOVICI and V. TH. BENTE (*Bull. Sci. Acad. Roumaine*, 1915, **4**, 185—194).—Chloral and bromal condense with phenylaminoacetonitrile and its methoxy-derivative with the elimination of hydrogen chloride or bromide and water and the formation of derivatives of 1 : 4-diazine [pyrazine). Thus chloral condenses with phenylaminoacetonitrile in anhydrous ether, the action being violent at first and completed on the water-bath. On cooling, the product sets solid, and by extraction with alcohol 2 : 3-*dichloro*-6-*phenylpyrazine* (annexed formula) is obtained in slender, silky, golden-yellow crystals, m. p. 102°. With alcoholic sodium or potassium hydroxide the crystalline substance turns first green, then blue, violet, and finally brown. On acidifying at any stage the solution turns deep red, the colouring matter being extractable with ether.



With *o*-methoxyphenylaminoacetonitrile, chloral yields under similar conditions 2 : 3-*dichloro*-6-o-*methoxyphenylpyrazine*,

$$C_{11}H_8ON_2Cl_2,$$

yellow, silky crystals, m. p. 144°.

Bromal condenses with phenylaminoacetonitrile to give 2 : 3-*dibromo*-6-*phenylpyrazine*, $C_{10}H_6N_2Br_2$, yellow, silky needles, m. p. 120°, and with *o*-methoxyphenylaminoacetonitrile to give 2 : 3-*dibromo*-6-*methoxyphenylpyrazine*, $C_{11}H_8ON_2Br_2$, m. p. 160°.

W. G.

An Oxidation Product of Indigotin. P. Friedländer and N. Roschdestwensky (*Ber.*, 1915, **48**, 1841—1847).—Indigotin, 6 : 6′-dibromoindigotin, and other indigoid dyes to a varying degree undergo atmospheric oxidation in hot solution in high-boiling solvents, such as ethyl benzoate, quinoline, ethyl phthalate, or phenanthrene; thus 1 gram of indigotin can be completely oxidised in half an hour when in solution in 20—30 grams of boiling phenanthrene. In the last case a small quantity of a yellow oxidation product was isolated, which proved to be identical with the compound $C_{15}H_8O_2N_2$ obtained by A. G. Perkin (P., 1906, **22**, 198) by subliming indigotin in the presence of air, and also with the compound wrongly described as $C_{16}H_8O_2N_2$, obtained by the oxidation of indigotin or isatin with neutral potassium permanganate solution (Meister, Lucius, & Brüning, D.R.-P. 1913, 281050 and 276808).

This oxidation product is reducible by sodium hyposulphite to a deep brown vat, which, when freshly prepared, is not affected by the air, but after some time at 100° becomes capable of oxidation to indigotin on account of the formation of indoxyl, and not of indigo-white as stated earlier (D.R.-P., *loc. cit.*). Reduction with acidic stannous chloride solution converts the substance into the *hydrochloride* (needles) of an easily oxidisable, feebly basic, reduction product. The presence of a carbonyl group also receives demonstration from the formation of an *oxime*, pale yellow needles, m. p. 265° (decomp.), and a *phenylhydrazone*, orange yellow needles, m. p. 242°. With sodium methoxide solution the substance gives a colourless solution containing a *sodium* derivative (colourless crystals), whilst with a very concentrated solution a violet-blue solution is obtained, from which violet-black needles (probably of a *disodium* derivative) may separate. Aqueous alkalis effect a simple fission into isatin and anthranilic acid according to the equation:

$$C_{15}H_8O_2N_2 + 2H_2O \longrightarrow NH_2\cdot C_6H_4\cdot CO_2H + C_6H_4{<}\genfrac{}{}{0pt}{}{CO-}{NH}{>}CO.$$

Of the possible condensation products of isatin and anthranilic acid it is possible to prove that the substance under investigation is *anhydro-α-isatinanthranilide*, $\begin{array}{l}CO\text{---}C{=}N \\ \vert \qquad\ \vert \\ C_6H_4\cdot N\cdot CO\end{array}{>}C_6H_4$, derived from α-isatinanthranilide, $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{N}{>}C\cdot NH\cdot C_6H_4\cdot CO_2H$, by ready elimination of water. The proof was effected by synthesis. When anthranilic acid and isatinanil are heated together in solution in acetic acid, *α-isatinanthranilide* is obtainable as an intermediate

yellow product, but if the solution is treated with a dehydrating agent, such as a mixture of sulphuric and acetic acids, yellow needles, m. p. 261°, of anhydro-α-isatinanthranilide are obtained. The latter substance is also produced by the interaction of anthranilic acid and isatin chloride in boiling xylene solution and by the condensation of *o*-nitrosobenzoic acid with indoxyl in feebly alkaline solution.

The yellow form of α-isatinanthranilide is probably to be represented by the constitution given above, whilst the violet-blue compound obtained by the action of excess of sodium methoxide solution on its anhydride is in all probability a sodium or disodium derivative of the structure $C_6H_4<{CO-\atop NH}>C:N\cdot C_6H_4\cdot CO_2H$.

D. F. T.

Some Aminoazimino-bases and Azo-dyes Derived from them. O. KYM and M RINGER (*Ber.*, 1915, **48**, 1671—1685).—Compounds of the type of aziminobenzene [1:2:3-benztriazole] (I) have been studied in order to determine whether they are at all analogous to the similar benziminazoles (II).:

$$C_6H_4<{NH\atop -N}\geqslant N \qquad C_6H_4<{NH\atop -N}\geqslant CH$$

(I.) (II.)

The azo-dyes obtained from a monoamino-derivative are found to combine directly with cotton, but not so well as the corresponding iminazole compounds, and it is also found that if the imino-group is substituted, even by a system containing another diazotisable amino-group, the dyes obtained are lighter in colour (compare A., 1904, i, 453; 1911, i, 1044). Other derivatives of the azimino-compcunds, such as acetyl compounds, have also been studied.

3:5-Dinitro-*o*-cresol was converted into 3:5-dinitro-*o*-toluidine by heating with carbamide, and this was reduced by sodium sulphide to 5-*nitro*-2:3-*tolylenediamine*, $NO_2\cdot C_6H_2Me(NH_2)_2$, which crystallised in orange-red, felted needles, m. p. 185°. This was converted by warm acetic anhydride into 5-*nitro*-2:3-*diacetyltolylenediamine*, $C_{11}H_{13}O_4N_3$, pale yellow needles, m. p. 234°, by boiling glacial acetic acid into 5-*nitro*-2:7-*dimethylbenziminazole*,

$$NO_2\cdot C_6H_2Me<{NH\atop -N}\geqslant CMe,$$

glistening needles, m. p. 186°, and by boiling formic acid into 5-*nitro*-7-*methylbenziminazole*, $NO_2\cdot C_6H_2Me<{NH\atop -N}\geqslant CH$, white needles, m. p. 199—200°. When heated with carbamide at 160—170°, the diamine yielded 5-*nitro*-2-*hydroxy*-7-*methylbenziminazole*, $NO_2\cdot C_6H_2Me<{NH\atop -N}\geqslant C\cdot OH$, which crystallises in silky needles, m. p. 329—330°, and forms a brick-red sodium salt. The diamine was also treated with sodium nitrite in cold hydrochloric acid solution, and thus converted into 5-*nitro*-7-*methyl*-1:2:3-*benztriazole*, $NO_2\cdot C_6H_2Me<{NH\atop -N}\geqslant N$, which was precipitated in pale yellow needles, m. p. 252—253°. This was reduced by stannous

chloride to 5-*amino-7-methyl*-1 : 2 : 3-*benztriazole*, glistening tufts of brown needles, m. p. 161—162°, which yielded the 5-*acetylamino*-compound, $C_9H_{10}ON_4$, glistening needles, m. p. 283°, when boiled with sodium acetate and acetic anhydride, and the 1 : 5-*diacetyl* derivative, $NHAc\cdot C_6H_2Me<\genfrac{}{}{0pt}{}{NHAc}{\underline{\quad\quad}N}>N$, silvery needles, m. p. 239—240°, when shaken with cold sodium hydroxide and acetic anhydride. The second acetyl group was eliminated by boiling with water (compare the acetyl derivative of benziminazole, A., 1913, i, 105).

5-Nitrodiacetyl-*m*-tolylenediamine was warmed for a short time with iron filings and 5% acetic acid, and so reduced to the 5-amine, m. p. 252—253° (Maron, A., 1911, i, 1032). This was converted by the action of nitrous acid into 1-*acetyl*-6-*acetylamino*-5-*methyl*-1 : 2 : 3-*benztriazole*, $NHAc\cdot C_6H_2Me<\genfrac{}{}{0pt}{}{NHAc}{\underline{\quad\quad}N}>N$, which separated like snow, in very slender needles, m. p. 220°, and was hydrolysed by boiling water to 6-*acetylamino*-5-*methyl*-1 : 2 : 3-*benztriazole*, m. p. 235°. The elimination of the 1-acetyl group also occurred when the diacetyl compound was boiled with nitrobenzene or pyridine, and the group could be re-introduced by the Schotten-Baumann reaction. The hydrolysis of the remaining acetyl group was effected by evaporation with hydrochloric acid. 6-*Amino*-5-*methyl*-1 : 2 : 3-*benztriazole*, $C_7H_8N_4$, was obtained in glistening needles, m. p. 173°, which dissolved in acids or alkali hydroxides.

2 : 4-Dinitrochlorobenzene was condensed with *m*-nitroaniline, and the trinitrodiphenylamine so obtained was reduced by sodium sulphide to 4 : 3′-*dinitro-2-aminodiphenylamine*, $C_{12}H_{10}O_4N_4$, red needles, m. p. 207—208°, which formed an *acetyl* derivative, in long, golden-yellow needles, m. p. 205°. When warmed with acetic anhydride and a few drops of sulphuric acid, the base underwent condensation to 5-*nitro*-1-m-*nitrophenyl*-2-*methylbenziminazole*, $NO_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{—N\cdot C_6H_4\cdot NO_2}{N:CMe}$, which formed silvery needles, m. p. 226—227°, and on treatment with nitrous acid it yielded 5-*nitro*-1-m-*nitrophenyl*-1 : 2 : 3-*benztriazole*, $NO_2\cdot C_6H_3<\genfrac{}{}{0pt}{}{—N\cdot C_6H_4\cdot NO_2}{N:N}$, yellowish-brown needles, m. p. 181°. This was reduced by carefully treating it with stannous chloride, and 5-*amino*-1-m-*aminophenyl*-1 : 2 : 3-*benztriazole*, $C_{12}H_{11}N_5$, was obtained in pale brown needles, m. p. 214—215°, which formed a *diacetyl* compound, lustrous scales, m. p. 248—249°.

The two isomeric aminoazimino-compounds and the above diamino-derivative were diazotised and coupled with β-naphthol, aminonaphthalenedisulphonic acid, or α-naphtholsulphonic acid, and the dyes were applied in 1% solutions to cotton. Neither dye is completely absorbed from solution by the cotton. J. C. W.

Two New *N*-Arylnaphthatriazoles. F. Elter (*Gazzetta*, 1915, **45**, ii, 312—316. Compare Charrier, A., 1910, i, 287).—

as-m-*Xylylazo-β-naphthylamine*, $NH_2\cdot C_{10}H_6\cdot N:N\cdot C_6H_3Me_2$, prepared from β-naphthylamine and *as-m*-xylenediazonium chloride, forms shining, pale red plates, m. p. 126°, and dissolves in concentrated sulphuric acid, giving an intense wine-red coloration.

2-as-m-*Xylylnaphthatriazole*, $C_{10}H_6<\overset{N}{\underset{N}{|}}>N\cdot C_6H_3Me_2$, obtained by heating the preceding compound, crystallises in rosettes of elongated, white leaflets, m. p. 85°, and dissolves in the cold in concentrated sulphuric acid, giving a greenish-yellow coloration.

α-Naphthaleneazo-β-naphthylamine, $NH_2\cdot C_{10}H_6\cdot N:N\cdot C_{10}H_7$, forms wine-red needles with green, metallic lustre, m. p. 154°, and dissolves in concentrated sulphuric acid, giving an intense wine-red solution. When heated, it yields

2-α-*Naphthylnaphthatriazole*, $C_{10}H_6<\overset{N}{\underset{N}{|}}>N\cdot C_{10}H_7$, which crystallises in short, thin, white needles, m. p. 163°, and in cold concentrated sulphuric acid gives a yellow solution.

m-Tolueneazo-β-naphthylamine, $NH_2\cdot C_{10}H_6\cdot N:N\cdot C_6H_4Me$, forms an orange-red, crystalline powder, m. p. 89°, and yields a wine-red solution in concentrated sulphuric acid. T. H. P.

s-Diantipyrylcarbamide and its Physiological Properties. MAXIMILIAN GÖTTLER (*Ber.*, 1915, **48**, 1765—1770).—In an endeavour to prepare antipyrylcarbamyl chloride by the action of carbonyl chloride on 4-aminoantipyrine, the author has obtained *s*-diantipyrylcarbamide.

When a toluene solution of carbonyl chloride is added to a solution of 4-aminoantipyrine in the same solvent at 50°, there is obtained a bulky, yellow to red precipitate, which on further heating and treatment with sodium carbonate yields s-*diantipyrylcarbamide*, $C_{23}H_{24}O_3N_6$, a pale yellow, crystalline powder, m. p. 259—260°; there can also be obtained from the toluene mother liquor a small quantity of a yellow oil, probably antipyrylcarbamyl chloride, which is converted by alcohol into antipyrylurethane. The probable course of the reaction is the primary formation of an additive compound, $\begin{matrix} CMe\cdot C(NH_2) \\ \| \\ NMeCl-NPh \end{matrix}>CO\cdot CO_2\cdot C<\begin{matrix} C(NH_2)\cdot CMe \\ \| \\ NPh-NMeCl \end{matrix}$, which is converted into the carbamyl chloride or carbamide derivative by the action of more carbonyl chloride.

Diantipyrylcarbamide does not readily form crystalline salts; it gives a *hydriodide*, $C_{23}H_{24}O_3N_6,1\frac{1}{2}HI,EtOH$ (from alcohol), olive green needles, m. p. 225—226°, or m. p. 210—211° if alcohol-free, and even in traces gives a red coloration with ferric chloride in the absence of much free acid. In the general manner of *s*-disubstituted carbamides, diantipyrylcarbamide reacts with primary aromatic amines; thus with aniline at 170°, vigorous interaction occurs, with formation of ammonia and *phenyl-s-diantipyrylcarbamide*, $C_{11}H_{11}N_2\cdot NH\cdot CO\cdot NPh\cdot C_{11}H_{11}N_2$, a crystalline mass, m. p. 240—241° (decomp.); treatment with phenylhydrazine at 190—195° gave this same compound together with red needles of a *substance*,

m. p. 158°, whilst at 170° a *compound*, m. p. 161—162°, was obtained. p-*Tolyl-s-diantipyrylcarbamide*,

$$C_{11}H_{11}N_2\cdot NH\cdot CO\cdot N(C_6H_4\cdot Me)\cdot C_{11}H_{11}N_2,$$

obtained with *p*-toluidine by a process similar to that for its phenyl analogue, forms slender needles, m. p. 235°. With *p*-phenetidine at 180°, the product was p-*ethoxyphenyldiantipyrylcarbamide*, $C_{11}H_{11}N_2\cdot NH\cdot CO\cdot N\cdot(C_6H_4\cdot OEt)\cdot C_{11}H_{11}N_2$, crystals, m. p. 234—235°; the corresponding *methoxy*-compound formed slender needles, m. p. 200°.

When heated with diethylmalonyl chloride in chloroform solution, diantipyrylcarbamide is converted into 1 : 3-*diantipyryl*-5 : 5-*diethylbarbituric acid*, $CO<\begin{matrix}N(C_{11}H_{11}N_2)\cdot CO\\N(C_{11}H_{11}N_2)\cdot CO\end{matrix}>CEt_2$, needles with a satin-like lustre, m. p. 312—313°. This substance has no basic properties and, unlike the above aryl derivatives and diantipyrylcarbamide itself, has no antipyretic action, and is also hypnotically inactive. D. F. T.

The So-called Pentazole Compounds of I. Lifschitz. TH. CURTIUS, AUGUST DARAPSKY, and ERNST MÜLLER (*Ber.*, 1915, **48**, 1614—1634).—Many attempts have been made to prepare pentazole, N_5H, or derivatives containing the five-nitrogen ring, but always without success (compare Hantzsch and Dimroth). Recently, however, Lifschitz has treated cyanotetrazole with hydrazine hydrate and obtained a compound which he designates "pentazolylacetohydrazidine" (A., 1915, i, 465), but many of the results described in this communication are so surprising that the present authors have repeated the work. They have come to the conclusion that the observations and deductions made by Lifschitz are erroneous.

When cyanogen is passed into aqueous azoimide for the preparation of cyanotetrazole (A., 1912, i, 144), a considerable but varying amount of a product of a further condensation with azoimide, namely, bistetrazole, is formed, thus: $N_3H + C_2N_2 \longrightarrow CHN_4\cdot CN$; this $+ N_3H \longrightarrow C_2N_8H_2$. On treating such a mixture with hydrazine hydrate in absolute alcohol at 0°, a white product separated at once, which was the *bishydrazonium* salt of *bistetrazole*, $\begin{matrix}N{-}N\\ \| \\ N\cdot NH\end{matrix}>C\cdot C<\begin{matrix}N{-}N\\ \| \\ NH\cdot N\end{matrix},2N_2H_4$, for the aqueous solution yielded benzaldazine on shaking with benzaldehyde. It formed white needles, m. p. 230°. On boiling the filtrate from this salt under reflux, ammonia was evolved, and the product solidified to a mass of yellow crystals. This was again warmed with hydrazine hydrate to complete the reaction, and when the evolution of ammonia had ceased there remained an orange-yellow mass. This is the product which Lifschitz called "pentazolylacetohydrazidine," $N_5\cdot CH_2\cdot C(:NH)\cdot NH\cdot NH_2$, but it is really the *bishydrazonium* salt of *ditetrazyldihydrotetrazine*,

$$CN_4H\cdot C<\begin{matrix}N{-}{-}N\\NH\cdot NH\end{matrix}>C\cdot CN_4H,2N_2H_4,$$

for the aqueous solution gives a precipitate of benzaldazine when shaken with benzaldehyde, and a solution of the theoretical amount of hydrazine hydrochloride and a precipitate of the free tetrazole compound on acidifying with hydrochloric acid. The free *ditetrazyldihydrotetrazine*, $C_4H_4N_{12}$, was obtained with $2H_2O$, which it lost at 130°, and it was easily reconverted into the hydrazine salt. The latter gave no ammonia on boiling with concentrated potassium hydroxide, as Lifschitz supposed, but hydrazine hydrate and the corresponding pale yellow *dipotassium* salt, and the acidic substance liberated from this by acetic acid was not "pentazolylacetohydrazide," but the free ditetrazyldihydrotetrazine. The presence of tetrazole residues in this was proved by the isolation of silver tetrazole from the product of an alkaline fusion, and by hydrolysis with concentrated hydrochloric acid to tetrazole and hydrazine.

When ditetrazyldihydrotetrazine was suspended in cold water, rendered alkaline with sodium carbonate, then mixed with sodium nitrite and at once acidified with acetic acid, the *disodium* salt of *ditetrazyltetrazine*, $C_4N_{12}Na_2,2H_2O$, separated in orange-red crystals, from which dilute sulphuric acid, but not acetic acid, liberated the free *ditetrazyltetrazine*, $CN_4H\cdot C{<}^{N.N}_{N:N}{>}C\cdot CN_4H$. This crystallised from alcohol in carmine-red, hexagonal leaflets or large needles. It could also be obtained by oxidising the dihydro-compound with cold chromic acid. When boiled with dilute aqueous or alcoholic hydrochloric acid, it lost nitrogen (1 mol. N_2 from 2 mols.) and, in part, yielded ditetrazyldihydrotetrazine again. Lifschitz supposed the product of the action of nitrous acid to be "pentazolyloximinoacetohydrazide," and the hydrolysis product "pentazolyloximinoacetic acid."

The behaviour of acetonitrile towards hydrazine has been studied again in the light of the above experiments (compare Curtius and Dedichen, 1894—1895). Acetonitrile and anhydrous hydrazine were boiled for a few days under reflux, when ammonia was evolved. The product was evaporated in a vacuum, when *dimethyldihydrotetrazine*, $CMe{<}^{N——N}_{NH\cdot NH}{>}CMe$, remained. This crystallised with $1H_2O$, which it slowly lost in a desiccator, and then on heating at 110—188° changed into 1-amino-2 : 5-dimethyltriazole,

$$NH_2\cdot N{<}^{CMe:N}_{CMe:N}.$$

Under the above conditions, the dimethyldihydrotetrazine was oxidised by nitrous acid to dimethyltetrazine, which was obtained by sublimation in beautiful, large, red needles, m. p. 74° (Pinner, 1897), and the aqueous solution was reduced again by hydrogen sulphide. J. C. W.

Formation of Mono- and Bis-azo-compounds from Phenols and their Ethers. K. VON AUWERS and E. BORSCHE (*Ber.*, 1915, **48**, 1716—1730. Compare A., 1914, i, 744).—In the earlier paper

it was shown that the ability of phenols to couple with diazonium salts is increased by the presence of alkyl substituents, particularly in the meta-position. Tri- and tetra-alkyl phenols have since become available, and they have therefore been examined in the same way. The coupling power of these is as pronounced as that of the dialkylphenols, but the phenolic ethers combine slightly less readily when they contain a third alkyl substituent and scarcely at all when there are four such groups present. As the methyl and ethyl ethers of the phenols were the only ones to be studied originally, the *iso*propyl, *tert*-butyl, and allyl ethers of *m*-5-xylenol have now been examined. They all couple as well as the methyl ether. In connexion with certain theoretical aspects of the coupling process, it was tested whether the formation of aminoazo-compounds from amines is influenced by an alkyl group in the meta-position. The three xylidines were examined, but such an influence could not be established.

m-5-Xylenol was heated with *iso*propyl alcohol, sodium *iso*propoxide (1 equiv.), and *iso*propyl bromide (1·5 equivs.) in a sealed tube at 100°, when m-5-*xylyl* iso*propyl ether*, $C_6H_3Me_2{\cdot}OPr^\beta$, was obtained as an oil, b. p. 208—210°. This was coupled with azophor-red, when it formed 2-p-*nitrobenzeneazo*-m-5-*xylyl* iso*propyl ether*, $NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_2Me_2{\cdot}OPr^\beta$, in brownish-violet needles, m. p. 92—93°. The corresponding *allyl ether*, b. p. 109°/11 mm., gave a brownish-red, crystalline *compound*, m. p. 102—103°, when coupled with azophor-red.

iso-ψ-Cumenol was also converted into the *methyl ether* (2:3:5-*trimethylphenyl methyl ether*), b. p. 213—216°, and this gave a 4-p-*nitrobenzeneazo*-compound, $OMe{\cdot}C_6HMe_3{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2$, in glistening, brownish-red leaflets, m. p. 130—132°.

o-Acetyl-*m*-5-xylenol (5-hydroxy-*m*-xylyl 4-methyl ketone) (this vol., i, 35) reacted slowly with an alkaline diazobenzene solution, giving 5-*hydroxy*-2-*benzeneazo*-m-*xylyl* 4-*methyl ketone*, $COMe{\cdot}C_6HMe_2(OH){\cdot}N{:}NPh$, slender, orange needles, m. p. 94°, and the 2:6-*bisbenzeneazo*-compound, glistening, brown needles, m. p. 169—170°, the former being soluble in 2% sodium hydroxide. The methyl ether gave no azo-dye. The hydroxy-ketone was reduced by Clemmensen's method to 3:5-*dimethyl*-2-*ethylphenol* (4-*ethyl*-m-5-*xylenol*), which formed glistening, flat needles, m. p. 80—81°, and the *methyl ether* of this had b. p. 110°/10 mm. The phenol yielded 4-*benzeneazo*-3:5-*dimethyl*-2-*ethylphenol*, brilliant red, flat needles, m. p. 119—120°, and the 4:6-*bisbenzeneazo*-compound, golden-brown needles, m. p. 148—149°, whilst the ether was converted into 4-p-*nitrobenzeneazo*-3:5-*dimethyl*-2-*ethylphenyl methyl ether*, $C_{17}H_{19}O_3N_3$, glistening, brownish-red needles, m. p. 120—121°.

The above allyl ether of *m*-5-xylenol was rearranged by heating (Claisen and Eisleb's recent method) into 3:5-*dimethyl*-2-*allylphenol* (4-*allyl*-m-5-*xylenol*), which formed slender, white needles, m. p. 50·5°, b. p. 135—136°/17 mm., and yielded a *methyl ether*, b. p. 116°/10 mm. The phenol gave a 4-*benzeneazo*-compound, rosettes of stout, red needles, m. p. 94—95°, and a 4:6-*bisbenzene*-

azo-derivative, violet-brown, felted needles, m. p. 132—133°, whilst the ether yielded the 4-p-*nitrobenzeneazo*-compound,

$$C_3H_5\cdot C_6HMe_2(OMe)\cdot N{:}N\cdot C_6H_4\cdot NO_2,$$

bluish-brown needles, m. p. 94—94·5°.

4:6-Diacetyl-*m*-5-xylenol (*loc. cit.*) was also converted into the *methyl ether*, $C_6HMe_2Ac\cdot OMe$, glistening prisms, m. p. 71—72°, but this would not couple with azophor-red. The diketone was reduced by Clemmensen's amalgamated zinc method to 3:5-*dimethyl*-2:6-*diethylphenol* (4:6-*diethyl*-m-5-*xylenol*), which crystallised in flat needles, m. p. 88°, and formed a *methyl ether*, b. p. 116—118°/10 mm., and an *ethyl ether*, a yellow oil, b. p. 254—255°. The phenol gave a 4-*benzeneazo*-derivative, glistening, red needles, m. p. 126—128°, and a 4-p-*nitrobenzeneazo*-compound, $OH\cdot C_6Me_2Et_2\cdot N{:}N\cdot C_6H_4\cdot NO_2$, brown needles, m. p. 168—170°.

The favourable influence of an alkyl group in the meta-position on the coupling power of a phenolic ether is also exerted in the case of dihydric phenols. Thus, orcinol methyl ether forms a p-*nitrobenzeneazo*-compound, $OMe\cdot C_6H_2Me(OH)\cdot N{:}N\cdot C_6H_4\cdot NO_2$, dark red needles, m. p. 225—226°, and the dimethyl ether also couples with azophor-red to give the *compound*, $C_{15}H_{15}O_4N_3$, silky, reddish-brown needles, m. p. 100—101°.

The p-*benzeneazo*-compounds derived from the three xylidines, $NH_2\cdot C_6H_2Me_2\cdot N{:}NPh$, are as follows: from *m*-5-xylidine, thin, red needles, m. p. 67°; from *m*-2-xylidine, tufts of brown needles, m. p. 99—101°; from *o*-3-xylidine, stout, ruby-red prisms, m. p. 96·5—97·5°. J. C. W.

Phthaleins. IV. Bisbenzeneazophenolphthalein. BERNARDO ODDO (*Gazzetta*, 1915, **45**, ii, 186—197).—The author has repeated Schestakov and Nocken's work on the action of a diazotised solution of aniline on phenolphthalein (A., 1914, i, 335), and has found that under no experimental conditions is it possible to obtain the compound, m. p. 189—190°, described by these authors. In all cases the resultant product is bisbenzeneazophenolphthalein, m. p. 234—235°, which forms a diacetyl derivative, m. p. 204° (compare A., 1913, i, 1110). T. H. P.

Action of Diazonium Salts on Anthranol. L. OMARINI (*Gazzetta*, 1915, **45**, ii, 304—312).—By the action of the corresponding diazonium salts on anthranol, the author has prepared various substituted hydrazones of anthraquinone. These compounds and their *N*-methyl ethers are readily hydrolysed by dilute acids to anthraquinone and arylhydrazones, and the same products are yielded by the action of an ethereal solution of nitric acid; incipient hydrolysis is observed on crystallisation from alcohol. Less satisfactory yields of the arylhydrazones are obtained by the interaction of the arylhydrazines and dibromoanthrone. Anthraquinone arylhydrazones mostly crystallise well and dissolve in aqueous alcoholic solutions of alkali hydroxides, giving intense blue colorations, but their *N*-methyl ethers, that is, anthraquinone arylmethylhydrazones, are insoluble in such alkali solutions (com-

pare Käufler and Suchannek, A., 1907, i, 225; Meyer and Zahn, A., 1913, i, 536; Charrier, A., 1915, i, 904).

Anthraquinone o-*tolylhydrazone*, $C_{21}H_{16}ON_2$, forms dense, dark red leaflets, m. p. 151—152°, and dissolves in concentrated sulphuric acid with an intense blue coloration, which changes to wine-red. The o-*tolylmethylhydrazone*, $C_{22}H_{18}ON_2$, forms small, garnet-red prisms, m. p. 126°, and is dissolved by concentrated sulphuric acid, giving a bluish-green coloration, changing to olive green and then to yellow. The p-*tolylhydrazone* crystallises in heavy, garnet-red leaflets, m. p. 173°, and gives an intense blue and then a wine-red coloration when dissolved in concentrated sulphuric acid. The p-*tolylmethylhydrazone* forms heavy, bright red leaflets, m. p. 179°, and is soluble in concentrated sulphuric acid, giving an emerald green and then a yellow coloration. The as-m-*xylylhydrazone*, $C_{22}H_{18}ON_2$, forms slender, orange-red leaflets, m. p. 170—171°, and gives a blue and then a wine-red coloration in sulphuric acid. The p-*chlorophenylhydrazone*, $C_{20}H_{13}ON_2Cl$, forms yellow, prismatic needles, m. p. 201—202°. The p-*chlorophenylmethylhydrazone*, $C_{21}H_{15}ON_2Cl$, forms shining leaflets with green, metallic lustre or a scarlet powder, m. p. 203°, and gives a bluish-green coloration, changing to yellow, in concentrated sulphuric acid. The α-*naphthylhydrazone*, $C_{24}H_{16}ON_2$, forms deep garnet-red prismatic needles with green, metallic lustre or a garnet-red powder, m. p. 155°. The α-*naphthylmethylhydrazone*, $C_{25}H_{18}ON_2$, forms garnet-red prisms, m. p. 158—160°, with previous softening. T. H. P.

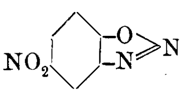
Attempts to Prepare Analogues to the Indazoles from Closed-chain Compounds, by means of Nitro- and Bromonitro-*o*-anisidines. E NOELTING and F. STEIMLE (*Bull. Soc. chim.*, 1915, [iv], **17**, 389—399).—The authors have studied the decomposition in acid solution of the diazo-compounds obtained from certain anisidine derivatives with the view of preparing substances analogous to the indazoles by the elimination of acid. Of the substances studied, two bromonitro-*o*-anisidines have not yet been described.

3:5-*Dibromo*-4-*nitro*-o-*anisidine*, $OMe\cdot C_6HBr_2(NO_2)\cdot NH_2$, is prepared by adding 4-nitro-*o*-anisidine in solution in acetic acid to bromine in acetic acid, the product being poured into water and crystallised from alcohol. It is obtained in orange leaflets, m. p. 102°. With acetic acid and acetic anhydride it gives an *acetyl* derivative, yellow needles, m. p. 182°.

3-*Bromo*-5-*nitro*-o-*anisidine* is prepared by adding bromine in glacial acetic acid to a cooled solution of 5-nitro-*o*-anisidine in the same solvent. The hydrobromide of the bromo-base separates and is decomposed by washing with water. The bromoanisidine gives yellow crystals, m. p. 140—141°, and furnishes an *acetyl* derivative, m. p. 204—205°. The acetyl derivatives of these two compounds give in aqueous or alcoholic solution with one drop of potassium hydroxide solution an intense yellow coloration.

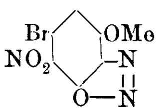
When the diazo-compound from 4-nitro-*o*-anisidine is allowed to remain in dilute sulphuric acid solution in the cold for several months there is no evolution of nitrogen, but a brown, crystalline compound slowly separates, which explodes at 118°, and is shown

to be Griess's nitrodiazophenol (annexed formula). When treated



with cuprous chloride in hydrochloric acid solution it yields 2-chloro-4-nitrophenol, m. p. 110°. When coupled with 2 : 6-naphtholsulphonic acid it yields a dull, reddish-brown compound, which with potassium dichromate turns brownish-black. The original diazo-compound under these conditions gives a bluish-red compound, which is not altered by treatment with potassium dichromate. If the original diazo-solution in sulphuric acid is warmed, the greater portion of the nitrogen is evolved, but a small amount of the nitrodiazophenol is formed. This formation of nitrodiazophenol does not take place if the anisidine is diazotised in acetic acid solution and then warmed or kept in the cold.

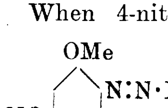
When 3 : 5-dibromo-4-nitro-*o*-anisidine is diazotised in either sulphuric acid or acetic acid solution, and the resulting solution allowed to remain in the cold, orange needles slowly separate, m. p. 189°, which detonate a few degrees above this temperature. In the formation of this *compound*, one bromine atom has been replaced by a hydroxyl group, which has then coupled with the diazo-group, with the elimination of acid. The probable constitution of this compound is as in the annexed formula.



It couples with 2 : 6-naphtholsulphonic acid, giving a coloured compound, changed by potassium dichromate.

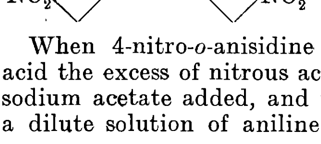
5-Nitro-*o*-anisidine when diazotised in sulphuric acid loses its nitrogen either in the cold or on heating, giving nitroguaiacol. 3-Bromo-5-nitro-*o*-anisidine, diazotised in sulphuric or acetic acid solution, loses all its nitrogen on warming, and if kept in the cold remains unaltered, even after three months.

4 : 5-Dinitro-*o*-anisidine when diazotised in acetic acid solution



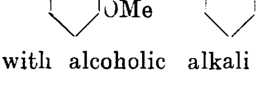
quickly yields in the cold the diazophenol (annexed formula) (compare Meldola and Eyre, T., 1902, **81**, 988), which by the action of cuprous chloride in hydrochloric acid solution gives 4-*chloro*-6-*nitro*-3-*methoxyphenol*, crystalling in white needles, m. p. 93°, giving an orange-red *potassium* salt and an orange-yellow *sodium* salt.

When 4-nitro-*o*-anisidine is diazotised in cold glacial acetic



acid solution, the *diazoamino*-compound (annexed formula) rapidly separates. It crystallises in microscopic, yellow prisms, m. p. 205° (decomp.).

When 4-nitro-*o*-anisidine is diazotised in cold dilute sulphuric acid the excess of nitrous acid destroyed by carbamide, an excess of sodium acetate added, and the solution filtered, and to the filtrate a dilute solution of aniline acetate added, 5-*nitro*-2-*methoxydiazoaminobenzene* (annexed formula) slowly



separates and crystallises from alcohol in orange needles, m. p. 123°.

Both these diazoamino-compounds give with alcoholic alkali hydroxides brownish-red alkali salts, dis-

sociated by water. When warmed with an excess of acetic anhydride they both lose the whole of their diazo-nitrogen.

W. G.

Optical and certain other Properties of Proteins. I. (contd.) M. A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1330. Compare A., 1915, i, 1015).—The adsorption of the albumin of hens' eggs by alumina is an irreversible process. T. H. P.

Adsorption of Solutions of Casein by Alumina. M. A. RAKUZIN and G. D. FLIER (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1331—1332).—According to the results obtained by Hammarsten, Osborne, and especially by Robertson, casein is a perfectly definite chemical individual, exhibiting constant physical properties and constant stoicheiometric relations to bases and acids. Unlike the albumin of hens' eggs and the peptone obtained from it (compare A., 1915, i, 1015, 1018), casein should therefore not be resolvable by the action of alumina. This conclusion is in accord with the actual behaviour. After two successive treatments with 10% of alumina for twenty-four hours, the specific rotation of a solution of casein in 2% borax solution was found to have the respective values $-95{\cdot}1°$ ($c_1=3{\cdot}68$) and $-94{\cdot}9°$ ($c_2=2{\cdot}95$), the original value being $-95{\cdot}5°$ ($c=5{\cdot}0204$); alumina does not adsorb borax from its solutions. The adsorption of casein by alumina is an irreversible process. T. H. P.

Hydratation and "Dissolution" of Gelatin. MARTIN H. FISCHER (*Kolloid. Zeitsch.*, 1915, **17**, 1—7).—The phenomenon of the liquefaction of gels has been examined in a comparative series of experiments in which 2 c.c. of a 10% gelatin gel was mixed with 8 c.c. of water or an equal volume of a solution of an electrolyte of varying concentration and kept at 25° for about twenty-four hours. The results obtained show that hydrochloric acid and sodium hydroxide have a very pronounced influence on the liquefaction of the gel in that the gel liquefies more and more readily as the concentration of the acid or alkali is increased.

For dilute solutions of acid or alkali hydroxides, the effect of the addition of salts is to counteract the liquefying tendency of the acid or base. For a given concentration of dilute hydrochloric acid, sodium chloride has a maximum effect at a definite concentration, and if this is exceeded the salt effect becomes smaller. Other salts behave similarly to sodium chloride, and the results obtained with potassium chloride, bromide, nitrate, iodide, thiocyanate, sulphate, citrate, and tartrate show that the last-mentioned salts produce the greatest effect.

The observations are said to support the view that hydratation of the protein gels consists in the combination of the proteins with water and that "dissolution" (liquefaction) corresponds with an increase in the degree of dispersity of the colloid. Biological applications of the phenomenon are discussed from this point of view.

H. M. D.

Rotatory Powers and Adsorption of α- and β-Gelatins. M. A. Rakuzin and (Mlle.) Ek. Maks. Braudo (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1333—1336).—α-Gelatin was converted into β-gelatin by Framm's method (A., 1898, i, 98). These two modifications have virtually identical specific rotations, and are both adsorbed positively and irreversibly by alumina. β-Gelatin is adsorbed negatively by α-gelatin. Both forms give the biuret reaction, but not Millon's, Adamkiewicz's, or the xanthoprotein reaction.

T. H. P.

Influence of Certain Capillary-active Substances on Enzyme Activity. Otto Meyerhof (*Intern. Zeitsch. phys.-chem. Biol.*, 1915, **2**, 394—396. Compare Chapman, A., 1915, i, 92).—Polemical. The difference between the results obtained by Chapman and those already recorded by Meyerhof (A., 1914, ii, 450) is to be ascribed to the difference in the mode of experimentation. H. W. B.

Introduction of the Guanidine Group into the Molecule of Polypeptides. II. A. Clementi (*Gazzetta*, 1915, **45**, ii, 276—280. Compare A., 1915, i, 77).—The action of the pancreatic juice of the dog and of the intestinal mucus of the dog and calf on guanidinoglycylglycine has been studied by the formaldehyde titration method. The results show that neither pancreatic trypsin nor intestinal erepsin is capable of hydrolysing this polypeptide. This seems to be the first case known in which a modification introduced artificially into the molecular constitution of a polypeptide renders it insensitive to the action of intestinal erepsin. T. H. P.

Action of Pectase. Nigel G. Ball (*Sci. Proc. Roy. Dubl. Soc.*, 1915, [N.S.], **14**, 349—357).—The action of pectase on a solution of pectin results in the formation of a gel, and not merely a very viscous liquid, the electrical conductivity remaining practically constant. The activity of the enzyme is much greater at 14° than at 0°.

The viscosity increases slowly at first, then more rapidly until a maximum is reached, after which there is a decrease. The decrease is accounted for by the action of the electrolytes, resulting in a suspension. N. H. J. M.

Action of Poisons on an Enzymatic Process. IV. Alkaline Earths, Acids, Metallic Salts. C. G. Santesson (*Chem. Zentr.*, 1915, ii, 751—752; from *Skand. Arch. Physiol.*, 1915, **33**, 97—152. See also A., 1915, i, 728).—Inorganic acids with the exception of boric acid inhibit in various degrees the action of muscle catalase. Nitric acid is most harmful, then phosphoric, sulphuric, and hydrochloric acids in the order named. Alkaline earth and magnesium salts are somewhat depressing, magnesium sulphate the least. Mercuric chloride, silver nitrate, and manganese sulphate are purely depressing, the latter, however, but feebly, and with indications of the reverse action at low concentration. Salts of copper, zinc, and iron, which of themselves act catalytically on hydrogen

peroxide, exert a more or less depressing action on muscle catalase according to their concentration. By superposition of both processes the evolution of oxygen decreases with decrease in concentration, increasing again with weak salt solutions and approaching the normal value. In solutions of medium concentration copper and zinc salts generate considerably more gas in presence of the enzyme than they would by themselves. Iron salts, on the other hand, exhibit the reverse phenomenon. Potassium fluoride exerts an unexpectedly small depression on the catalase action.

G. F. M.

New Heterocyclic Systems. I. Analogues of Piperidine in which the Nitrogen Atom is Replaced by Phosphorus, Arsenic, Antimony, or Bismuth. GERHARD GRÜTTNER and MAXIMILIAN WIERNIK (*Ber.*, 1915, **48**, 1473—1486).—The authors have succeeded in preparing penta-, hexa-, and hepta-atomic ring-systems containing, in addition to carbon, one of the elements phosphorus, arsenic, antimony, bismuth, silicon, tin, lead, and thallium. The present paper includes only the hexatomic rings containing the first four elements. The general method of preparation was to submit the organo-magnesium derivative of $\alpha\epsilon$-dibromopentane or of the corresponding chloro-compound to the action of a compound of the type $RXHal_2$, where X represents the element to be introduced and R a univalent organic radicle. The simple cyclic nature of the products is shown by their normal molecular weights and the readiness with which the chlorine additive compounds undergo fission, yielding $\alpha\epsilon$-dichloropentane. The b. p.'s of the products confirm von Braun's result that the replacement of two ethyl groups by a pentamethylene chain is accompanied by a rise of approximately 50° in the b. p.

The organo-magnesium derivative of $\alpha\epsilon$-dibromopentane reacts readily with phosphenyl chloride, $PPhCl_2$, in ethereal solution; after evaporation of the solvent, the residue was distilled under reduced pressure, when *phenyl*cyclo*pentamethylenephosphine*, $CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>PPh$, a colourless oil of characteristic odour, b. p. 143—144°/16—18 mm. (in carbon dioxide), $D_4^{21\cdot6}$ 1·0306, n_D^{20} 1·5886, was obtained; *mercurichloride*, $C_{11}H_{15}P,HgCl_2$, m. p. 172° (decomp.); *methiodide*, slender, colourless crystals, m. p. 188°. The compound also reacts vigorously with carbon tetrachloride, giving a hygroscopic, colourless *additive* product.

p-*Tolyl*cyclo*pentamethylenephosphine*, $C_5PH_{10}\cdot C_6H_4Me$, obtained by an analogous process to the last, is a similar compound, b. p. 167—168°/24 mm. (in carbon dioxide), D_4^{20} 1·0007, $n_D^{22\cdot2}$ 1·5729; when treated in light petroleum solution with chlorine it gives, first a colourless, crystalline solid, and then an oil, the latter being decomposed by distillation under reduced pressure with formation of $\alpha\epsilon$-dichloropentane. *Mercurichloride*, needles, m. p. 157°; *methiodide*, a pale yellow oil; *ethiodide*, crystals, m. p. 163—164°. The new base also gives an *additive* compound with carbon tetrachloride.

*Phenyl*cyclo*pentamethylenearsine*, $C_5AsH_{10}Ph$, obtained by the

action of dichlorophenylarsine on the organomagnesium compound in ethereal solution, is a colourless, rather viscous oil of unpleasant odour, b. p. 153—154°/18-20 mm. (in carbon dioxide), D_4^{20} 1·2480, $n_D^{21·4}$ 1·5944, which was also obtained, but in poorer yield, by the interaction of $\alpha\epsilon$-dibromo-(or dichloro-)pentane, dichlorophenylarsine, and sodium in the presence of ether; the *dichloride*, $C_{11}H_{15}AsCl_2$, obtained by the action of chlorine on a solution in carbon tetrachloride, is an exceedingly hygroscopic substance, leaflets, m. p. 138—139°, which, when distilled under a pressure of 20 mm., regenerates $\alpha\epsilon$-dichloropentane; the *dibromide* is an oil; the *di-iodide*, pale yellow crystals, and the *tetraiodide*, a brown oil; the *mercuriacetate*, $C_{11}H_{15}As,Hg(OAc)_2$ (needles), obtained by mixing the components, when treated with a methyl-alcoholic solution of calcium chloride, is converted into the *mercurichloride*, $C_{11}H_{15}As,HgCl_2$, needles, m. p. 201·5—202°, which can also be obtained by mixing alcoholic solutions of the components; *methiodide*, colourless leaflets, m. p. 179·5°; *ethiodide*, prisms, m. p. 185°; n-*propiodide*, crystals, m. p. 137—138°; iso*propiodide*, crystals; n-*butiodide*, crystals, m. p. 140°.

p-*Tolyl*cyclo*pentamethylenearsine*, $C_6H_4Me·C_5AsH_{10}$, prepared with the use of dichloro-*p*-tolylarsine, is a colourless oil of rather unpleasant odour, b. p. 162—163°/20 mm. (in carbon dioxide), D_4^{20} 1·2174, n_D^{20} 1·5948; *dichloride*, needles, m. p. 134°, converted by alcohol into the hydroxide, and by distillation into 1:5-dichloropentamethylene; *mercurichloride*, needles, m. p. 175°.

*Phenyl*cyclo*pentamethylenestibine*, $C_5SbH_{10}Ph$, obtained in the general manner from dichlorophenylstibine, is a colourless, rather viscous oil of faint, unpleasant odour, b. p. 169—171°/18—20 mm. (in carbon dioxide), D_4^{20} 1·4966, $n_D^{22·4}$ 1·6203, which on exposure to the air for a few hours at the ordinary temperature is converted into *phenyl*cyclo*pentamethylenestibine oxide*, a colourless powder, unfused at 280°; *dichloride*, needles, m. p. 141—142°.

*Ethyl*cyclo*pentamethylenebismuthine*, EtC_5BiH_{10}, prepared from dibromoethylbismuthine, is a pale yellow, viscous oil, b. p. 108—112°/18—20 mm. (in carbon dioxide), of very unpleasant, persistent odour; it oxidises rapidly in the air, and paper wetted with it soon inflames. D. F. T.

m-Aminophenolarsinic Acid and its Reduction Products. Hugo Bauer (*Ber.*, 1915, **48**, 1579—1583).—When m-aminophenol is heated with arsenic acid it suffers oxidation to dark-coloured products, and, similarly, the acetyl derivative is first hydrolysed and then oxidised. The carbethoxy-compound, however, as has already been mentioned (A., 1915, i, 606), is more stable, and gives rise to 4-carbethoxyamino-2-hydroxyphenylarsinic acid, the constitution of which is established by a synthesis from 3-nitro-6-aminophenol. The acid has been further hydrolysed to 4-amino-2-hydroxyphenylarsinic acid, and this reduced to 4:4′-diamino-2:2′-dihydroxyarsenobenzene, which, although isomeric with "salvarsan," has no great therapeutic value.

m-*Carbethoxyaminophenol*, $OH·C_6H_4·NH·CO_2Et$, is obtained

almost quantitatively by adding ethyl chloroformate to a solution of *m*-aminophenol in ethyl acetate, filtering the hydrochloride of the base, which separates at once, and evaporating the filtrate. It has m. p. 97°. For the "arsination," the compound was heated with 83% arsenic acid for a week, when the solid mass was washed free from arsenic acid and purified through the ammonium salt, which is sparingly soluble in concentrated ammonia solution. 4-*Carbethoxyamino-2-hydroxyphenylarsinic acid*,

$$CO_2Et\cdot NH\cdot C_6H_3(OH)\cdot AsO_3H_2,$$

decomposes at 213°, and is hydrolysed by boiling sodium hydroxide to 4-*amino-2-hydroxyphenylarsinic acid*, $C_6H_8O_4NAs$, m. p. 173°. The two compounds were reduced by means of stannous chloride and a little hydriodic acid, or hypophosphorous acid and potassium iodide, and 4 : 4′-*diamino-2 : 2′-dihydroxyarsenobenzene*,

$$[NH_2\cdot C_6H_3(OH)]_2As_2,$$

was obtained as a yellow precipitate and a pale yellow, soluble hydrochloride.

The original 4-carbethoxyamino-2-hydroxyphenylarsinic acid was synthesised as follows: 3-Nitro-6-aminophenol was diazotised and converted by means of sodium arsenite (Barth, A., 1913, i, 115) into 4-*nitro-2-hydroxyphenylarsinic acid*, $C_6H_6O_6NAs$, which was purified through the insoluble magnesium salt, and obtained in crystals, decomposing at about 250°. This was reduced by boiling with iron filings and acetic acid, and the alkaline filtrate was then treated with ethyl chloroformate. The desired acid was then precipitated as the magnesium salt by "magnesia mixture."

J. C. W.

Arsenical Acids Derived from Thiophen. I. Cesare Finzi (*Gazzetta*, 1915, **45**, ii, 280—290).—The methods for preparing aromatic arsenic derivatives given by Béchamp (*Compt. rend.*, 1863, **56**, 1172. Compare also Ehrlich and Bertheim, A., 1907, i, 812) and by Bart (A., 1913, i, 115) give unsatisfactory results when applied to thiophen derivatives. It is found, however, that mercury 2 : 2′-dithienyl (compare Steinkopf and Bauermeister, A., 1914, i, 427) reacts with arsenic trichloride with generation of heat, and that oxidation of the product of this reaction by hydrogen peroxide in alkaline solution yields thiophen-2-arsinic acid, which exhibits all the properties characteristic of the primary arylarsinic acids (compare Michaelis, A., 1902, i, 411). In this preparation the mercury 2 : 2′-dithienyl may be conveniently replaced by thiophen 2-mercurichloride (compare Volhard, A., 1892, 828; Steinkopf and Bauermeister, *loc. cit.*).

Thiophen-2-arsinic acid, $C_4H_3S\cdot AsO(OH)_2$, forms tufts of needles, m. p. 135·5°, and at 105—108° is converted into the corresponding anhydride. By a current of sulphur dioxide in presence of a trace of hydriodic acid it is reduced to thiophen-2-arsenious oxide, $C_4H_3S\cdot AsO$, whilst with sodium hyposulphite it yields arseno-2-thiophen, $C_4H_3S\cdot As{:}As\cdot C_4H_3S$. The acid and its derivatives do not give the colour reaction of thiophen with a sulphuric acid solution

of isatin. The *sodium hydrogen, magnesium, barium hydrogen,* and *silver* salts were prepared.

Di-2-thienylarsinic acid, $(C_4H_3S)_2AsO_2H$, obtained as a secondary product in the preparation of thiophen-2-arsinic acid, and in better yield by heating thiophen-2-arsinic trichloride with thiophen-2-mercurichloride in a sealed tube, forms groups of minute needles, m. p. 172°. T. H. P.

Arsenical Acids Derived from Thiophen. II. C. FINZI and VITTORIA FURLOTTI (*Gazzetta*, 1915, **45**, ii, 290–298. Compare preceding abstract).—*5-Nitrothiophen-2-arsinic acid,*

$$NO_2\cdot C_4H_2S\cdot AsO(OH)_2,$$

prepared by the action of nitric and sulphuric acids on thiophen-2-arsinic acid in the cold, forms small prisms, and if heated rapidly melts with spluttering and conversion into anhydride at 194°; with slow heating, however, the anhydride is formed without melting, and remains solid above 250°. When reduced by means of sodium amalgam or sodium hyposulphite, it yields *5-aminothiophen-2-arsinic acid,* $C_4H_4NS\cdot AsO(OH)_2$, which forms tufts of pale yellow, microscopic laminæ, undergoes profound decomposition at 194°, and is readily diazotised and subsequently condensed with amines and phenols, forming highly coloured compounds; its *hydrochloride* was prepared.

5-Acetylaminothiophen-2-arsinic acid, $NHAc\cdot C_4H_2S\cdot AsO(OH)_2$, forms white prisms, m. p. 134° (decomp.) with rapid heating.

Di-5-nitrodi-2-thienylarsinic acid, $(NO_2\cdot C_4H_2S)AsO\cdot OH$, forms brownish-red, microscopic crystals, m. p. 287° (decomp.), and gives a brownish-red coloration when heated with alkali hydroxide.

T. H. P.

Arseno-Metallic Compounds. P. EHRLICH and P. KARRER (*Ber.*, 1915, **48**, 1634—1644).—An account of the chemistry of a class of compounds that has already been the subject of many patents (compare A., 1914, i, 345, 761, 1010; 1915, i, 728).

The best known arseno-compound, namely, 3:3′-diamino-4:4′-dihydroxyarsenobenzene, "salvarsan," by the exertion of two residual affinities, has the power of combining with two molecules of a metallic salt to form a complex. The number of the residual affinities of the metallic component do not seem to play an important part, for similarly constituted compounds containing copper, silver, gold, mercury, palladium, platinum, iridium, ruthenium, and osmium are already known. Moreover, all the arseno-compounds investigated, including arsenobenzene itself, form these complex salts, which points to the conclusion that the arsenic atoms alone provide the connecting links with the metallic atoms.

The tendency to the formation of the complexes is so great that it is possible to obtain them under remarkable conditions. If, for example, a reducing agent, such as a hyposulphite or hypophosphorous acid, is added to a solution of an arsinic acid and a metallic salt, the latter is not reduced to the metal, but combines at once with the arseno-compound which results from the reduction of the arsinic acid.

Since each arsenic atom exerts an additive power, it might be supposed that compounds containing only one proportion of a metallic salt should exist. Unfortunately, most of the complex salts scarcely differ from the arseno-compounds in solubility and are just as difficult to crystallise, but the cupric chloride compounds with one and two molecules of the metallic salt combined with one molecule of "salvarsan" are both comparatively soluble and have been obtained pure.

The therapeutic value of the metallic complexes is often greater than that of "salvarsan." Thus, the compound with $1CuCl_2$ is remarkably effective against trypanosomes, and has the additional advantage that the curative dose is only about 15% of the lethal dose.

The *compound*, $C_{12}H_{12}O_2N_2As_2,2HCl,CuCl_2$, is precipitated when a methyl-alcoholic solution of cupric chloride (35·8 grams in 400 c.c.) is stirred into a methyl-alcoholic solution of "salvarsan" hydrochloride (100 grams in 1600 c.c.) containing a little hydrogen chloride. The precipitation is completed by pouring into ether. It is an orange powder, moderately soluble in water, readily so in glycerol and 2*N*-sodium hydroxide. The *compound* with $2CuCl_2$ is very similar. The *compounds*, $C_{12}H_{12}O_2N_2As_2,2HCl$, $2AgNO_3$, and $1AgNO_3$, prepared in a similar manner, are yellowish-brown and very soluble, except in ether. The *compound* with $HgCl_2$ is a yellow, granular powder which is less stable towards water than the compound with HgI_2. The gold chloride *compound* is brownish-yellow, the platinum chloride *compound* is brown, and the palladium *compound* is almost black.

The arsines and arsenoxides also contain tervalent arsenic atoms and should be capable of similar reactions. However, the latter compounds, R·AsO, show little activity, and the residual affinity of the arsenic atom is strongly influenced by substituents in the nucleus, whilst the former, $R·AsH_2$, although the residual affinity is very great, are such powerful reducing agents that the metallic complexes can only exist for a few moments. J. C. W.

Preparation of Derivatives of Bismethylaminotetramino-arsenobenzene Substituted in the Nucleus, Soluble in Water. C. F. BOEHRINGER & SÖHNE (*Eng. Pat.* 8759, 1915; from *J. Soc. Chem. Ind.*, 1915, **34**, 1072).—Instead of converting bismethylamino-tetraminoarsenobenzene into the soluble carbamate by the action of an alkali or ammonium hydrogen carbamate, its derivatives substituted in the nucleus are treated in this way, giving almost neutral yellow to brown solutions of therapeutic value, stable in absence of oxygen. G. F. M.

Organic Antimony Compounds. I. The Action of Antimony-Trichloride on Triphenylstibine (GERHARD GRÜTTNER and MAXIMILIAN WIERNIK (*Ber.*, 1915, **48**, 1749—1759. Compare this vol., i, 93).—Having found that the earlier reports on the interaction of antimony trichloride and triphenylstibine are conflicting (com-

pare Hasenbäumer, A., 1899, i, 209; Michaelis and Günther, A., 1911, i, 1056; Morgan and Micklethwaite, T., 1911, **99**, 2286; May, T., 1912, **101**, 1033), the authors have reinvestigated this subject and have discovered that the discrepancies are almost entirely explained by the alteration effected in the composition of the reaction product during distillation.

In the interaction of triphenylstibine with antimony trichloride (approx. 2 mols.), it is found that although the former substance may be almost entirely consumed, a very considerable proportion of the latter remains unaltered, and can be extracted by cold 15%-hydrochloric acid. The equation $SbPh_3 + 2SbCl_3 = 3SbPhCl_2$ (Hasenbäumer, *loc. cit.*) cannot be correct. If the crude reaction product, from which excess of antimony chloride has been removed, is heated for four hours at 200—210° in an atmosphere of carbon dioxide, partial decomposition into antimony chloride and an organic compound poorer in chlorine occurs. The change is probably to be represented by the equation $2SbPhCl_2 = SbPh_2Cl + SbCl_3$.

In order to obtain a closer insight into the nature of the products of the interaction of antimony chloride and triphenylstibine, the authors heated triphenylstibine and antimony chloride with xylene in a closed tube at 240—245° for forty hours, and after removing the excess of antimony chloride by hydrochloric acid, distilled off the xylene under a pressure of 16—18 mm. A portion of the oily residue was treated with magnesium ethyl bromide in ethereal solution. A second portion was distilled in an atmosphere of carbon dioxide under 16—18 mm. pressure; after the removal of antimony chloride from this, a part was treated with magnesium ethyl bromide, whilst another part was again distilled and the previous treatment repeated. The behaviour of the three products thus obtained, during distillation showed that in the first the chief constituent was phenyldiethylstibine, but that the two subsequent operations successively caused a diminution in this constituent, so that the third product consisted mainly of diphenylethylstibine. These results indicate clearly that repeated distillation of dichlorophenylstibine, $SbPhCl_2$, causes gradual conversion into chlorodiphenylstibine and antimony trichloride, and the variation between the results obtained by earlier experimenters must be due to the different periods of distillation. Traces of hydrochloric acid appear to exert a very powerful catalytic effect on this decomposition.

The best yield of dichlorophenylstibine is obtained when 30 grams of triphenylstibine and 40 grams of antimony trichloride are heated with 18 c.c. of xylene for seventy-five hours at 240—245°, when approximately 70% of the organic product consists of this compound, the remainder consisting of chlorodiphenylstibine. A larger excess of antimony chloride does not increase the yield of the dichloro-compound, and the mechanism of the change is probably represented by the two equations $SbPh_3 + SbCl_3 = SbPhCl_2 + SbPh_2Cl$ and $SbPh_2Cl + SbCl_3 = 2SbPhCl_2$, the former being the more rapid and therefore the more effective. Prolonged heating or distillation diminishes the quantity of the dichloro-compound

produced, by causing a conversion into the monochloro-compound and antimony chloride.

The earlier statements that by cooling crude dichlorophenylstibine the substance crystallises (Hasenbäumer, also Morgan and Micklethwaite, *loc. cit.*) are improbable, because even after six months no crystalline deposit was obtained by the authors from the product richest in this compound, and the liquid nature of this substance at the ordinary temperature would be as expected by analogy with dichlorophenylarsine.

The physiological effect of the crude reaction product from antimony chloride and triphenylstibine in producing painful eruptions on the skin, as described by some of the earlier investigators, appears to be selective, some persons experiencing no ill effect.

In the course of this research, triethylstibine was found to have b. p. below 75°/16—18 mm., D_4^{16} 1·3244, and triphenylstibine b. p. 231—232°/16—18 mm., D_4^{12} 1·4998 (see also following abstract).

D. F. T.

Organic Antimony Compounds. II. Preparation of Mixed Aryl-alkyl Stibines. GERHARD GRÜTTNER and MAXIMILIAN WIERNIK (*Ber.*, 1915, **48**, 1759—1764. Compare preceding abstract).—By treating the crude product obtained by heating triphenylstibine and antimony chloride with xylene at 245—248° for five hours with magnesium methyl bromide in ethereal solution, the authors have obtained *phenyldimethylstibine*, $SbPhMe_2$, as a colourless, mobile liquid, b. p. 112°/16—18 mm. (in an atmosphere of carbon dioxide), D_4^{20} 1·4490, $n_D^{19·5}$ 1·5983. The substance fumes in the air and undergoes rapid oxidation, so that for the preparation of the following derivatives it was necessary to exclude air: *methiodide*, colourless needles, decomp. at 235° with liberation of iodine; *ethiodide*, colourless needles, decomp. at 150° with liberation of iodine; *chloride*, $SbPhMe_2Cl_2$, obtained by the action of chlorine on a solution in carbon tetrachloride, long, colourless prisms, m. p. 128°; *bromide*, $C_8H_{11}SbBr_2$, colourless tablets or prisms, m. p. 112—113°; *iodide*, $C_8H_{11}SbI_2$, very pale yellow, crystalline powder or stellar aggregates, m. p. 98·5—99°. If in the preparation of the last compound an excess of iodine is used, a dark, badly crystalline product is obtained.

Phenyldiethylstibine, $SbPhEt_2$, obtained in an analogous manner, is a colourless liquid, b. p. 128°/16—18 mm. (in carbon dioxide), D_4^{24} 1·3487, $n_D^{21·8}$ 1·5903, which fumes more strongly than the dimethyl compound, and sometimes inflames if exposed on a filter paper; the same precautions as before were therefore necessary in the preparation of derivatives. The *methiodide*, colourless needles, decomp. at 225°, after previous scission of iodine, was formed less readily than that of phenyldimethylstibine, and it was not found possible to produce an ethiodide; *chloride*, $C_{10}H_{15}SbCl_2$, a non-volatile, colourless oil; *bromide*, a non-volatile, colourless oil; *iodide*, pale yellow prisms (from ether) or hexagonal leaflets (from benzene), m. p. 88·5—89°.

Diphenylmethylstibine, $SbPh_2Me$, was prepared in an analogous

manner from chlorodiphenylstibine (Grüttner and Wiernik, preceding abstract; also Lettermann, Diss., 1911, Rostock); it is a colourless, rather viscous oil, b. p. 174—177°/16—18 mm. (in carbon dioxide), D_4^{20} 1·2134, n_D^{20} 1·6021, which does not fume in the air, but nevertheless undergoes rapid oxidation; *chloride*, $C_{13}H_{13}SbCl_2$, colourless prisms, m. p. 144°; bromide, colourless prisms, m. p. 148° (Lettermann, *loc. cit.*, gives 200°).

Diphenylethylstibine, $SbPh_2Et$, prepared in the same way as its methyl analogue, is a colourless, viscous oil, b. p. 190—192°/16—18 mm. (in carbon dioxide), $D_4^{19.5}$ 1·3541, $n_D^{20.5}$ 1·6309; *chloride*, $C_{14}H_{15}SbCl_2$, colourless platelets, m. p. 163—164°; *bromide*, monoclinic tablets, m. p. 158°. D. F. T.

Physiological Chemistry.

Relation between Temperature and Oxygen Consumption in the Animal Organism. ARISTIDES KANITZ (*Intern. Zeitsch. phys.-chem. Biol.*, 1915, **2**, 272—278. Compare Krogh, A., 1915, i, 97).—Polemical. The author shows that Krogh's results are in harmony with Arrhenius's law. H. W. B.

Pharmacology of the Respiratory Centre. II. ARTHUR R. CUSHNY and CHARLES C. LIEB (*J. Pharm. expt. Ther.*, 1915, **6**, 451—471).—Morphine slows respiration with little or no effect on its depth; urethane induces no change except that arising from general narcosis. Under morphine, carbon dioxide inhalation produces the usual results, both rate and depth of breathing being increased; under urethane, there is acceleration, but this diminishes as the dose of urethane increases. Lack of oxygen produces the same effects. The carbon dioxide concentration in the blood increases under urethane, and to a less degree under morphine, but this cannot be the cause of the reversed action of carbon dioxide under urethane. After rapid inflation of the lungs, the apnœic pause is lengthened under morphine, but only slightly under urethane. Morphine affects the intrinsic rhythm of the respiratory centre, but the centre is less depressed by urethane. In both cases the reaction to reflexes remains normal. In death from morphine, the rhythm of the centre is abolished, whilst in urethane poisoning the centre responds by slowing and finally by arrest, owing to the accumulation of carbon dioxide. Both drugs mainly act on the rhythm of the centre, but the depth of the breathing depends on the concentration of the carbon dioxide in the blood. W. D. H.

Combustion in the Lungs and the Estimation of the Blood Gases. V. HENRIQUES (*Biochem. Zeitsch.*, 1915, **71**, 481—491).—To get concordant results in blood analyses it is necessary that

the blood (oxalated or defibrinated) should be kept well agitated as it is withdrawn, so that the corpuscles do not settle. Analyses made on blood withdrawn in this manner are more satisfactory than on blood withdrawn slowly from animals with hirudin injections, as in this case there is a tendency of the corpuscles to sink in the connecting tubes, and the samples obtained are not therefore uniform. Blood withdrawn simultaneously from the right side of the heart and from the pulmonary artery contains the same amount of carbon dioxide and oxygen. The blood in the right side of the heart corresponds in composition, therefore, with that perfusing the lungs. Experiments were carried out in which the carbon dioxide excretion and oxygen consumption by the lungs were estimated at the same time as the gas-content of the blood passing to and the blood passing from the lungs. Before and after the experiment the rate of flow of the blood through the lungs was also estimated. The results do not support the conception of Bohr and Henriques of a special combustion process in the lungs.

S. B. S.

The Influence of Osmotic Pressure on the Volume of Red Blood-corpuscles and the Problem of Permeability. H. J. HAMBURGER (*Biochem. Zeitsch.*, 1915, **71**, 464—467).—The author claims that he was the first to call attention to the relationship between osmotic pressure and cell volume, and also that he was a pioneer in the investigations on the permeability of cells. These facts are not recognised in some of the most recent text-books.

S. B. S.

Biology of Phagocytes. Influence of Hydrogen Peroxide on Phagocytosis. H. J. HAMBURGER (*Intern. Zeitsch. phys.-chem. Biol.*, 1915, **2**, 255—265).—Hydrogen peroxide has a stimulating action on phagocytes suspended in serum or saline solution, which is made apparent by an increase in the number of phagocytes which ingest particles of starch or of charcoal suspended in the medium. If after treatment with hydrogen peroxide the phagocytes are well washed with saline solution before being brought into contact with the suspended particles, the enhanced phagocytosis is still observed. A similar action is not observed with other oxidising substances, such as potassium chlorate and potassium ferricyanide. The strength of the hydrogen peroxide employed was about 1 : 3000, and was shown to be incapable of causing disintegration of the inactive phagocytic cells. The enhanced phagocytosis was therefore absolute, and not merely apparent. H. W. B.

Fibrin and the Coagulation of the Blood. I., II. and III. E. HEKMA (*Intern. Zeitsch. phys.-chem. Biol.*, 1915, **2**, 279—298, 299—351, 352—369).—Historical survey. H. W. B.

The Effect of Chloroform on Coagulation. GEORGE R. MINOT (*Amer. J. Physiol.*, 1915, **39**, 131—138).—Antithrombin is rendered inactive by chloroform and ether, thus allowing free thrombin, if present in oxalated blood-plasma, to produce a clot. Prothrombin is not converted into thrombin by chloroform, neither does chloro-

form weaken the action of thrombin solutions; ether does slightly. Antithrombin could not be recovered from chloroform or ether extracts of serum or plasma. Chloroform can precipitate both fibrinogen and prothrombin from an oxalated plasma. In one rabbit poisoned with chloroform the antithrombin was decreased.

W. D. H.

Adaptation of Ferments. I. KOOPMAN (*Intern. Zeitsch. phys.-chem. Biol.*, 1915, **2**, 266—271).—The diastatic activity of the saliva in man remains the same whether the diet is restricted entirely to carbohydrates or consists largely of proteins or is a mixed one. The percentages of dry matter, of ash, chlorine, and nitrogen also remain fairly constant. The enzyme is inactivated by heating at 65° more quickly on the protein than on the other diets, whilst re-activation occurs only when the diet has consisted chiefly of carbohydrates (compare Gramenitzki, A., 1911, i, 98).

H. W. B.

The Acid of the Gastric Juice and Gastric Ulcer. CHARLES BOLTON (*J. Path. Bact.*, 1915, **20**, 133—158).—Experimental and clinical evidence is adduced that it is the acid, and not the enzyme, of gastric juice which produces and increases the necrotic condition of gastric ulcers. The damage done is in proportion to the strength of the acid; 0·3—0·4% is taken as evidence of hyperacidity.

W. D. H.

Metabolism of Amino-acids in the Organism. IX. UGO LOMBROSO (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 401—408).—The results previously obtained are summarised and discussed (compare A., 1915, i, 917).

The experiments with Ringer's solution, and still more those with blood, show that different amino-acids exhibit different behaviour, and that those which are utilised most by one tissue are least utilised by another. Thus, glycine is utilised well by functioning muscle, but less by the liver, whilst alanine is readily utilised by the kidneys and intestine, but not so well by muscle. It seems, therefore, that no particular amino-acids are generically better utilisable than others, but rather that each tissue exhibits specific selectivity with reference to the amino-acids; asparagine is, however, withdrawn in larger quantity from the circulating liquid, and shows a tendency to become deaminated.

The more or less marked disappearance of amino-acids observed in almost all experiments made with blood is not accompanied by the formation of such compounds as ammonia and acetone in quantities sufficient to justify the conclusion that such disappearance is due to deamination; complexes of the amino-acids are, therefore, probably formed. The experiments with Ringer's solution, especially in the intestine and liver, reveal the opposite tendency, that is, the withdrawal of amino-acids with formation of ammonia.

Since the ability of the liver to synthesise amino-acids by coupling

ammonia with the carbonyl group of ketonic compounds is known, it is evident that complex and antagonistic phenomena take place in the various tissues. T. H. P.

Influence of Calcium Salts on Reproduction. RUDOLF EMMERICH and OSKAR LOEW (*Landw. Jahr.*, 1915, **48**, 313—330; from *Chem. Zentr.*, 1915, ii, 717).—Experiments with mice, rabbits, and guinea pigs indicated that an increase of calcium in the diet led to an increased number of litters, and an increase in the number of individuals in each litter, accompanied by a decreased individual weight. Sodium chloride had a similar action, but the increased fertility of the animals resulted in this case in a great decrease in weight (12%) of the mother. Magnesium chloride was without action, and potassium chloride worked very unfavourably.
G. F. M.

The Effects of Aqueous Extracts of Organs on Unstriated Muscle. GEORGE G. FAWCETT, JESSIE M. RAHE, GEORGE S. HACKETT, and JOHN ROGERS (*Amer. J. Physiol.*, 1915, **39**, 154—161).—The residues (that is, aqueous extracts minus nucleo-proteins and coagulable proteins) of pituitary, pineal, thyroid, parathyroid, thymus and adrenal glands, liver, pancreas, and spleen contain most if not all of the internal secretions of these organs; each produces a characteristic stimulating effect on the plain muscle of the cat's uterus, which is paralysed by adrenaline. There are differences in the activity of the various extracts; each is supposed to act on some portion of the sympathetic nerve-endings by a different chemical or physico-chemical action. W. D. H.

The Feeding of Young Chicks on Grain Mixtures of High and Low Lysine Content. G. D. BUCKNER, E. H. NOLLAN, and J. H. KASTLE (*Amer. J. Physiol.*, 1915, **39**, 162—171).—Osborne and Mendel have shown that lysine is largely responsible for the stimulation of growth. The present experiments on various lots of chickens support this view. Analytical tables of the food supplied are given, the main difference being in the lysine content. Other conditions of rearing were kept constant. The failure to grow on a food mixture poor in lysine is strikingly shown by tables of body-weights and by photographs. This failure is not made good by adding growth-producing fat (butter) to the rations.
W. D. H.

Quantitative Observations on Antagonism. A. R. CUSHNY (*J. Pharm. expt. Ther.*, 1915, **6**, 439—450).—The experiments were performed with atropine and pilocarpine on the salivary secretion of dogs. In different dogs a constant amount of atropine was necessary to oppose the action of a constant amount of pilocarpine, and in the same dog the ratio of the two drugs remained the same, however much the actual amounts injected might vary; that is, the antagonism proceeded according to the laws of mass-action and not according to those of chemical combination. There was

evidence that when one poison had been allowed to act for some time its antagonist was less effective than if it had been injected simultaneously. W. D. H.

Kyrines. HANS FREUND (*Pharm. Zentr.-h.*, 1915, **56**, 663—667).—In extension of the work on blood proteins (A., 1914, i, 447), the author has examined some kyrines in order to determine whether they differ in toxicity from their parent proteins.

Pure globinokyrine sulphate was obtained from hæmoglobin and glutokyrine sulphate from gelatin by the usual processes, which are described. These were injected intravenously and subcutaneously into rabbits and guinea-pigs, and were found to be less toxic than the parent globin or gelatin. J. C. W.

Antiphenol Serum. (MLLE.) JANINA WISZNIEWSKA (*Compt. rend.*, 1915, **161**, 609—612).—Dogs fed on meat preserved by artificial methods and rendered aseptic by a careful process of tyndallisation show an increase of phenols in the animal economy. In this process of putrefaction important variations are noticed, due to the quality of the ingested food. With a basal diet of albumin and protein substances, *p*-hydroxyphenylacetic acid is found in the urine to the extent of 0·004—1·5 grams per litre. A dog fed on decomposed meat shows after the seventh day an average of 1·619 grams of phenol in the urine. In the case of dogs under normal conditions, carefully fed so as to avoid intestinal putrefaction, on administering *p*-hydroxyphenylacetic acid in small doses it is found that the phenols are eliminated without being fixed in the tissues.

An attempt was made to isolate phenols resulting from putrid intoxication, and an amorphous substance was obtained which did not pass through a dialyser membrane. It gave the biuret reaction and showed the general characteristics of the leucomaines, whilst yielding some reactions peculiar to phenols. It was strongly alkaline, and its toxic coefficient was fixed at 0·00012 per kilogram. It is thermostable. When fed to animals at intervals in suitable doses, it produced an intense sclerosis at the end of four or five months, particularly in the renal and cephalic arteries. When injected intravenously into a horse, it furnished characteristic antitoxins which could be used therapeutically. Animals immunised by means of this serum survived a five months' feeding with the substance mentioned above.

The following test is given for the phenol antigen. When a 0·1% solution of the antigen is mixed with a few drops of a solution of ethyl nitrite and a few drops of strong sulphuric acid, an intense red coloration is produced, which passes into blue on the addition of a few drops of ammonia. The red coloration can be detected at a dilution of 1 in 2,000,000. W. G.

Albuminuria Produced by Intravascular Injection of Ovalbumin. A. CH. HOLLANDE, M. LEPEYTRE, and J. GATÉ (*J. Pharm Chim.*, 1915, [vii], **12**, 345—350).—The physiological albuminuria following the intravascular injection of white of egg can be

differentiated from pathological albuminuria by means of Maurel's solution, which is a mixture of 25 c.c. of sodium hydroxide (33% solution), 5 c.c. of a 3% copper sulphate solution, and 70 c.c. of glacial acetic acid. This solution coagulates ovalbumin, whilst serum albumin and serum globulin are unaffected. Ovalbumin may also be distinguished from serum albumin by adding formaldehyde to the urine and then heating to the boiling point; serum albumin coagulates, whereas ovalbumin remains in solution.

H. W. B.

The Relationship between Toxic Dose and Body Surface. KARL KISSKALT (*Biochem. Zeitsch.*, 1915, **71**, 468—478).—From numerous experiments on the injection of caffeine into rats, the conclusion is drawn that Dreyer's statement as to the relationship between lethal dose and body surface does not hold true.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Comparative Effects of Phosphates and Sulphates on Soil Bacteria. E. B. FRED and E. B. HART (*Agric. Exper. Stat. Univ. Wisconsin, Research Bull.* 35, 1915).—Ammonification occurs with peptone in solutions, and with casein in soils, both with pure and mixed cultures.

Addition of potassium dihydrogen phosphate to peptone solution greatly increased the production of ammonia, especially at the end of the second day, whilst precipitated calcium phosphate stimulated ammonia production in five-day liquid cultures. With tricalcium phosphate, or bone-ash, there was no increase of ammonia in peptone solutions.

Calcium and potassium sulphates slightly increased ammonification, the latter being the more effective.

Addition of potassium dihydrogen phosphate results in an enormous increase in the numbers of bacteria, followed by a rise in ammonia production, which, however, is not in proportion to the number of bacteria.

In the soil experiments, dipotassium hydrogen phosphate stimulated ammonification and cell production, whilst tricalcium phosphate gave a slight increase. All phosphates, especially dipotassium phosphate, increased the numbers of bacteria.

Addition of sulphates and phosphates to soil increased the production of carbon dioxide; with ammonium sulphate the increase was very great.

The results indicate that the increased crop production following an application of soluble phosphates is partly due to increased bacterial activity. With increased ammonification the plants

obtain more available nitrogen, and with increased production of carbon dioxide more available mineral nutrients. N. H. J. M.

Further Investigations on the Proteolytic Activity of Lactic Organisms. I. Influence of the Temperature. CONSTANTINO GORINI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 369—376).—Further experiments confirm the author's previous result (*Ann. Micrographie*, 1897, **9**, 433) that the decompositions of the lactose and of the casein of milk by one and the same bacterium are related to the temperature conditions, the lactose being attacked preferably at a comparatively high temperature, whilst peptonisation of the casein occurs best at a low temperature. All functions of any given organism have therefore not the same optimum temperature. The supposed connexion between the morphology and the physiological activity of lactic organisms is found to be untenable.

T. H. P.

A New Nitrite-forming Organism. N. V. JOSHI (*Mem. Dept. Agric. India, Bact. Ser.*, 1915, **1**, 85—96).—The organism, which differs morphologically from those hitherto described, produces nitrites from ammonium salts, asparagine, and carbamide; in the case of ammonium carbonate and carbamide, the presence of calcium carbonate seems to retard the production of nitrites.

Carbon dioxide, up to 50%, and coal-gas stimulate the organism, whilst dextrose (0·1 gram) and asparagine (0·2 gram in 50 c.c. of Omelianski's solution) have retarding effects. Magnesium carbonate is much less effective than calcium carbonate as a base for nitrite formation by the organism.

The thermal death point of the organism is between 70° and 80°, and the optimum temperature between 25° and 35°.

N. H. J. M.

The Assimilation of Carbon Dioxide. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Ber.*, 1915, **48**, 1540—1564).—The first portion of an investigation on the assimilation of carbon dioxide, dealing with the relation between the chlorophyll content and the assimilatory activity of leaves. The method of experiment was to pass a current of air containing a known amount of carbon dioxide through a small illuminated glass chamber containing 5—20 grams of leaves, at constant temperature, and to determine the carbon dioxide in the issuing gas; a correction was made for the quantity of carbon dioxide found to be yielded by the leaves to a similar stream of air in the dark.

It is found that the ratio of chlorophyll content to assimilatory effect is not a constant one, the most marked cases being with autumnal green leaves, the assimilatory effect of which is relatively low, and with leaves of yellow varieties poor in chlorophyll and etiolated leaves regaining their green colour, which possess high assimilatory power. During the spring growth of the leaves also a gradual diminution occurs in the ratio of carbon dioxide assimilated per hour to chlorophyll-content, a similar difference also being observable in the comparison of young and old leaves.

These results are attributed to the existence of another factor, probably enzymatic, in the assimilation process. In leaves rich in chlorophyll the rate of assimilation is almost independent of the degree of illumination within certain limits, probably because in this case the chlorophyll effect outweighs that of the enzyme; rise in temperature with normal leaves increases the assimilation, probably on account of the marked influence of temperature on the enzymatic process. With leaves poor in chlorophyll, temperature change between 15° and 30° causes little alteration in the assimilatory process, possibly owing to the enzyme exerting its full effect on the chlorophyll. The duty of the enzyme may be to facilitate the decomposition of an intermediate compound of chlorophyll and carbon dioxide with liberation of oxygen. D. F. T.

Swelling and Germination of Plant Seeds. I. TRAUBE and T. MARUSAWA (*Intern. Zeitsch. phys.-chem. Biol.*, 1915, **2**, 370—393).—The influence of non-electrolytes, salts, acids, and bases on the swelling of starchy seeds, such as barley, is essentially the same as that exerted on pure starch (see Samec, A., 1915, i, 76). Bases greatly increase the swelling, whilst indifferent narcotics, such as ethers and alcohols, have only a slight accelerating action. Glycerol, sugars, salts, acids, and the capillary-active higher fatty acids usually inhibit the imbibition phenomenon.

Peas and other seeds containing relatively larger quantities of protein are more affected by the added substances than starchy seeds. The narcotics have an inhibitory action on such seeds, possibly due to their coagulating action on the proteins.

The effect of the added substances on germination is usually determined by their action on the enzymes concerned in the germination processes. Indifferent narcotics anæsthetise the enzymes and delay germination, and, after the removal of the narcotic, germination may proceed undisturbed, although in many cases evidence of permanent injury is apparent. When acids are employed, germination and growth are usually permanently inhibited when a certain limit in concentration is overstepped. In minute traces, however, certain acids, such as citric acid, decidedly increase the rate of germination. The processes of germination and growth are often affected to different degrees by the added substances. The capillary-active higher fatty acids are specially injurious to germination.

The effects of numerous bases, salts, alkaloids, and dyes on germination and growth have also been studied. H. W. B.

Rate of Absorption of Various Phenolic Solutions by Seeds of Hordeum vulgare, and the Factors Governing the Rate of Diffusion of Aqueous Solutions across Semipermeable Membranes. ADRIAN J. BROWN and FRANK TINKER (*Proc. Roy. Soc.*, 1915, [*B*], **89**, 119—135. Compare A., 1909, ii, 386; 1912, ii, 1086).—Barley seeds were steeped in water and in $N/2$-phenolic solutions at 19° and at 32·2°, and in solutions of phenol of various strengths ($N/2$ to $N/32$) at 22·6°. The increase in weight was ascertained at intervals.

The results obtained with $N/2$-solutions at 19° showed a gradual falling off in the rate of absorption as the equilibrium point is reached. With the exception of pyrogallol, the phenols showed a marked accelerating effect, as compared with water, the greatest effect being produced by phenol, then by catechol, resorcinol, and quinol in the order as given. At the higher temperature absorption was much more rapid, and the equilibrium was attained in two or three days, instead of six or seven days. The relative rates with the different solutions remained, however, the same.

With the different concentrations of phenol, the rate of absorption decreases with increased dilution, and with the $N/32$-solution the results were practically the same as with water.

Estimations of the surface tensions of the phenolic solutions, at the different temperatures employed, showed a close relationship with the corresponding absorption constants, the order in magnitude of the latter being the same as the inverse order of the former; so that the product of the surface tension and the absorption constant is practically constant. The conclusion is drawn that when osmotic pressures, vapour pressures, and viscosities of a series of solutions of permeable solutes are equal, their rates of diffusion across the barley membrane are inversely proportional to their surface tensions. N. H. J. M.

Osmotic Pressure in Plants. IV. Constituents and Concentration of the Sap in the Conducting Tracts, and on the Circulation of Carbohydrates in Plants. HENRY H. DIXON and W. R. G. ATKINS (*Sci. Proc. Roy. Dublin Soc.*, 1915, [N.S.], **14**, 374—392).—In the sap in the tracheæ of the trees examined, mono- or di-saccharides, or both, are found at all times, usually in greater amounts than electrolytes. The greatest concentration of sugars occurs in the early spring, after which there is a rapid dilution, for which the rise in transpiration is largely responsible, so that a minimum concentration occurs in summer or autumn. Through the winter there is a rise in concentration, culminating in the vernal maximum, which coincides with the period of greatest root-pressure. The upward conveyance of carbohydrates, of which sucrose seems to be the most important, is a continual and primary function of the tracheæ; whilst the sheath of wood parenchymæ round the vessels functions as a gland to secrete carbohydrates into the rising transpiration stream.

The presence of large quantities of carbohydrates in the wood-sap of roots is probably responsible for root-pressure and bleeding.

In the evergreen *Ilex* and the sub-evergreen *Cotoneaster*, the concentration curves of solutes show smaller fluctuations than those of deciduous trees. The concentration of the carbohydrates is usually greater in the tracheæ of the stem than in the roots, except during the summer. In *Ilex*, however, the concentration in the root is the greater, except in winter.

The columns of the tracheids may be supposed to afford a permanent channel for the water and salts, and to a less degree for organic substances. N. H. J. M.

Osmotic Pressure in Plants. V. Seasonal Variations in the Concentration of the Cell-sap of some Deciduous and Evergreen Trees. HENRY H. DIXON and W. R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1915, [N.S.], **14**, 445—461).—The osmotic pressure of tissues is mainly due to dissolved carbohydrates, and the variations in the pressure are, to a great extent, caused by fluctuations in the amount of carbohydrates in the sap, and, in a smaller degree, to changes in the concentration of the electrolytes.

In the case of leaves there is a progressive rise in osmotic pressure, due to accumulation of electrolytes; whilst in the one root which was examined it was found to be due to the concentration of carbohydrates.

The osmotic pressure of *Syringa vulgaris* (deciduous) rose, irregularly from about 13 atm., at the opening of the buds, to a maximum of about 18 atm. in August.

In the case of the evergreens *Ilex aquifolium* and *Hedera helix* the osmotic pressure in the leaves was greater in the winter months than in the summer. The osmotic pressure of the sap in the roots of *I. aquifolium* rose from a minimum of about 6 atm. in October to a maximum of 14 atm. in September. There was no concentration of electrolytes in these roots due to age, and the increased osmotic pressure in the older roots is evidently due to increased concentration of the carbohydrates. N. H. J. M.

Studies in Permeability. II. Effect of Temperature on the Permeability of Plant Cells to the Hydrogen Ion. WALTER STILES and INGVAR JØRGENSEN (*Ann. Bot.*, 1915, **29**, 611—618).—From the results of experiments with potato discs the conclusion is drawn that the absorption of the hydrogen ion of hydrochloric acid in dilute solution by potato cells takes place according to a simple exponential relation between time and the concentration of the acid. The rate of absorption is increased about 2·2 times for a rise of 10° between 0° and 30°. N. H. J. M.

Presence in Plants of Hæmatoid Compounds of Iron. II. G. GOLA (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 289—294. Compare A., 1915, i, 926).—In order to obtain the hæmatoid compounds of iron of plants in a pure condition, advantage is taken of the solubility of their picrates. From these the picric acid may be removed by treatment with water or by solution in sodium hydrogen carbonate solution and subsequent acidification with acetic acid. A large number of vegetable organisms of different kinds have been examined, and the results show that the occurrence of organic compounds of iron may be regarded as general. The principal properties of these compounds are as follows: They are soluble in aqueous alkali solutions, but not in dilute acids, and they yield picrates soluble in neutral solvents, and are soluble in pyridine after they have been detached from the protein molecule. Their iron is removed by the action of aqueous alkali in the hot, but they are resistant to hot aqueous acids and to alkali even at 240°. With hot alcoholic hydrogen chloride they give compounds which

still contain iron and have some of the characters of hæmin. When heated with zinc dust or aluminium they yield pyrrole derivatives. It is probable, therefore, that plants contain iron compounds which are chemically and perhaps also biologically analogous to those characteristic of the blood pigments of many animals. T. H. P.

Pigments of Fruits in Relation to some Genetic Experiments on Capsicum Annuum. W. R. G. ATKINS and G. O. SHERRARD (*Sci. Proc. Roy. Dubl. Soc.*, 1915, [N.S.], **14**, 328—365).—In Capsicum fruits red is dominant to yellow, and seems to be a simple dominant to chocolate and orange. In unripe fruits the different shades of green are due to variations in the numbers of chromatophores in each cell.

The red and chocolate pigments form oily liquids, and also differ from lycopin, carotin, and xanthophyll by dissolving readily in cold alcohol and light petroleum. The solutions become colourless when evaporated in daylight.

The amount of peroxydase in the fruits seems to diminish during ripening. It is frequently present only in the epidermis, whilst the deeper tissues contain a strongly reducing inhibitor.

N. H J. M.

Content of Amylase in Ripening Seeds of Horse Beans. A. BLAGOVESCHTSCHENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1529—1532).—Examination of the seeds of *Vicia faba L. var. minor* at different stages of their maturation shows that the amount of amylase present changes approximately in the same way as the rate of accumulation of starch. This result is regarded as a proof of the synthesising action of the amylase in the ripening seeds, the apparent incompleteness of the parallelism between rate of synthesis and amount of enzyme being due to the loss of some of the starch from the assimilatory organs. T. H. P.

Oxydases and their Inhibitors in Plant Tissues. IV. The Flowers of Iris. W. R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1915, [N.S.], **14**, 317—327).—The peroxydase reactions of related species of *Iris* are similar, although the distribution and amount of anthocyanin may be very different. Active peroxydase is absent in the Pogoniris group, whilst the reactions are usually well marked in the Xiphion group; in the Apogon group the distribution varies.

When negative results are obtained by the usual method, the presence of the enzyme can be shown by treatment with hydrogen cyanide or toluene-water, which removes an inhibitor, probably by diffusion, since the protoplasm is rendered permeable by the reagents.

When the flowers are kept in darkness, the quantity of active peroxydase increases; in one case organic peroxide was produced.

It is not possible to correlate the distribution of peroxydase and anthocyanin in *Iris*, owing perhaps to complications introduced by inhibitors. N. H. J. M.

Formation of Alkaloids in Papaver Somniferum, L. var. Nigrum, and the Opium obtained from the Plant. L. VAN ITALLIE and J. A. VAN TOORENBURG (*Pharm. Weekblad*, 1915, **52**, 1601—1606).—The opium from *Papaver somniferum* var. *nigrum* contains thebaine, narceine, morphine, codeine, and papaverine, but not narcotine. A. J. W.

Odoriferous Substances of the Thorn-apple, Datura Stramonium. A. SIVOLOBOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1561—1569).—The products obtained on distilling disintegrated branches of *Datura stramonium*, including leaves, flowers, twigs, and fruit cones, with water consist principally of methyl and ethyl alcohols mixed with small proportions of trimethylcarbinol (?), aldehydes, ketones, and esters. The aldehydes comprise acetaldehyde and, probably, formaldehyde, propaldehyde, *iso*butaldehyde, and another of considerably higher boiling point. Acetone and another ketone of higher boiling point were found, and esters of acetic and formic acids. The small proportion of odoriferous substances is explainable by their volatility, which prevents any marked accumulation. T. H. P.

Soil Gases. J. WALTER LEATHER (*Mem. Dept. Agric. India, Chem. Ser.*, 1915, **4**, 85—134).—By means of an attachment to a soil-boring cylinder, the soil samples could be at once completely enclosed and the whole of the contained gases could be pumped out. In addition to the total volumes of gas, the amounts of argon, nitrogen, oxygen, hydrogen, and carbon dioxide were estimated. Argon was estimated because its ratio to the oxygen or nitrogen in soil gases would show whether these gases had been liberated or combined.

When rain falls on a dry soil, the volume of gas displaced is not necessarily the same as the volume of water. In the wettest weather it was found that the soil contained about half as much gas as in hot, dry weather.

Gases from swamp rice soils were found to contain large amounts of nitrogen in relation to argon, indicating liberation of soil nitrogen, very little oxygen, and considerable amounts of hydrogen and methane. Gases in the neighbourhood of roots contained high percentages of carbon dioxide, and commonly contained hydrogen, but not methane.

Analyses of gases from soils during active nitrification showed normal instead of low amounts of oxygen. These results, and others obtained in nitrification experiments in closed vessels, seem to point to a rapid diffusion of gases through soil.

The conclusion is drawn that tillage of the soil is unnecessary as far as aeration is concerned, and that the value of good cultivation must be due to other effects. N. H. J. M.

Adsorption of Potassium and Phosphate Ions by Typical Soils of the Connecticut Valley. ROBERT H. BOGUE (*J. Physical Chem.*, 1915, **19**, 665—695).—The adsorption of phosphate and potassium ions by four typical soils from the Connecticut valley

has been exhaustively studied. The soils examined were a Windsor sand, a Podunk fine sandy loam, a Connecticut meadow silt loam, and a Suffield clay. The soils were thoroughly leached with water to remove any soluble salts and then placed in a nickel tube, and solutions of potassium chloride and monocalcium orthophosphate, $CaH_4(PO_4)_2$, of known strength were allowed to percolate through them. The change in concentration of the potassium and phosphate ions was determined colorimetrically. The results of the investigation are expressed in tables and curves. The main results are in agreement with previous work of Cameron, Schreiner, Failyer, and Schloesing. It is shown that when soils are leached, the concentration of phosphate and potassium ions in the soil extract approaches a constant value, which appears to be fixed and definite for any given soil. When soils are subjected to the action of soluble potassium and phosphate salts, the concentration of these salts in the soil extract is at first not materially increased, owing to the power of the soils to adsorb these salts, but as adsorption proceeds it becomes weaker, and a point is finally reached where the amount of soluble salts extracted in the soil extract is nearly equivalent to the amount applied. The concentration of the potassium and phosphate ions in the soil extract approaches a low constant, which appears to be fixed and definite for each soil, when only a part of the adsorbed ions has been removed by the leaching action of water. The constants attained by the four soils by the leaching action of water are very nearly alike, which seems to indicate that the concentration of the potassium and phosphate ions in the soil solutions of the various soils were practically the same and not at all dependent on the amount of adsorbed potassium or phosphate they originally contained. This indicates that the concentration of salts in soils is largely dependent on the specific adsorptive capacity of the individual soils. These results tend to disprove the theory that the composition of the soil moisture, and hence the adsorptive capacity of the soil, is determined primarily by the composition of the soil. They tend to prove that this quality is dependent on the mechanical texture of the soil. Further, since these soils continue to adsorb small amounts of potassium and phosphate ions long after the approximate point of saturation has been reached, and they continue to lose potassium and phosphate ions in small amounts long after the soluble forms must have been entirely leached out, and as the latter point is reached long before all the previously adsorbed potassium and phosphate ions have been leached out, it would appear that the soils were able to take up these ions from the solution in two distinct ways: first, by saturating itself with the ions, these undergoing no chemical change, and thus remaining readily soluble and easily leached out; and, secondly, by interacting with the salts, producing insoluble compounds, which are slowly reconverted into soluble compounds on treatment with water. J. F. S.

Field Test with a Toxic Soil Constituent: Vanillin. J. J. SKINNER (*U.S. Dept. Agric. Bull.*, 164, 1915).—The results of pot

experiments in which clover was grown in soil containing 100 mg. per kilo. of vanillin, increased by subsequent additions to 300 mg., showed a reduction in yield of 53%. Similar experiments with wheat showed injurious effects in two soils (sand and sandy loam respectively), whilst in a third soil (loam) no injurious effects were observed.

Experiments were also made with different plants grown on small plots. The soil was a silty, clay loam of an acid nature with a low percentage of organic matter. Vanillin was applied the day before sowing the seed, and three other applications were made, the total amount added being 320 kilos. per hectare. The final results showed considerable reductions in the yields of cow peas, garden peas, and string beans.

It was found that the soil when kept for six months after the application of vanillin was still harmful to the respective crops.

N. H. J. M.

The Solubility of the Phosphoric Acid in Powdered Thomas Slag on Repeated Extraction with Water Containing Carbon Dioxide. J. G. MASCHHAUPT (*Chem. Zentr.*, 1915, ii, 552; from *Verslag. Landbouwkund. Onderzoek. Rykslandbouwproefstat.*, 1915, 41 pp.).—The amount of phosphoric acid which can be extracted from powdered Thomas slag by water containing carbon dioxide depends largely on the relative quantities of the solid and liquid phases. If this relation is fairly constant, the more marked is the effect of the free lime and calcium silicate present on the solubility of the phosphoric acid. Slag powder characterised by a high solubility with respect to citric acid gives a higher yield of phosphoric acid in the earlier extractions, but after a certain number of extractions all samples exhibit similar behaviour as to the solubility of the remaining phosphoric acid. The content of free lime determined by extraction with a sugar solution is higher in samples of low solubility towards citric acid, whilst the content of calcium silicate is higher in samples showing the same characteristic. The varying content of free lime can only in a small degree be responsible for the variable solubility in citric acid, because although the removal of the lime raises the percentage of phosphoric acid extracted by 2% citric acid or by water containing carbon dioxide, the differences still persist, and therefore are possibly to be referred to double salts of calcium silicate and calcium phosphate.

The results do not indicate any definite relation between the solubility in water containing carbon dioxide and in citric acid, considerable differences being observed in the behaviour on the first extraction with the former solvent with samples the difference between which is only slight as measured by the citric acid test.

D. F. T.

Organic Chemistry.

Preparation of Aluminium Ethoxide. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 286596; from *J. Soc. Chem. Ind.*, 1915, **34**, 1168).—Dry alcohol is treated with aluminium in the presence of a very small quantity of mercuric chloride (as a catalyst) and in the presence or absence of alkyl haloids or iodine. The mixture is then distilled under reduced pressure, when a distillate free from mercury is obtained. J. C. W.

Preparation of γ-Methylbutinol and its Homologues. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 285770; from *J. Soc. Chem. Ind.*, 1915, **34**, 1167).—The alkali compounds of acetylene or its homologues are treated with acetone or its homologues in an inert medium. J. C. W.

Simple and Mixed Alkyl Phosphates. W. A. DRUSHEL (*Amer. J. Sci.*, 1915, [iv], **40**, 643—648).—Trialkyl phosphates were prepared by the action of phosphoryl chloride on the corresponding sodium alkyloxides in suspension in dry ether. Contrary to statements in the literature, they were all, up to tri*iso*butyl phosphate, found to be distillable in a vacuum without decomposition. Although stable towards cold *N*/10-hydrochloric acid, they were readily hydrolysed by aqueous barium hydroxide, and from the barium salts of the dialkyl hydrogen phosphates produced mixed trialkyl phosphates were obtained by the silver salt method. The hydrolysis of the mixed trialkyl phosphates by barium hydroxide proceeds in two directions simultaneously, and not as stated by Lossen and Köhler (A., 1891, 1013) by the removal of one of the alkyl groups which occurs twice to the exclusion of the group that occurs only once, so that the product contains esters of the types $HRR'PO_4$ and HR_2PO_4. Tables are given showing the effect of various alkyl groups on the velocity constants of the hydrolysis of simple and mixed trialkyl phosphates by hydrochloric acid at 100°. The following physical constants are given for the phosphoric esters: Trimethyl, b. p. 197°/760 mm., D^{22} 1·200; triethyl, b. p. 215°/760 mm., D^{22} 1·056; tripropyl, b. p. 131°/15 mm., D^{22} 1·007; tri*iso*butyl, b. p. 152°/15 mm., D^{22} 0·965; dimethylethyl, b. p. 203°/760 mm., D^{22} 1·161; dimethylpropyl, b. p. 116°/15 mm., D^{22} 1·180; methyldipropyl, b. p. 129°/20 mm., D^{22} 1·059; diethylpropyl, b. p. 130°/20 mm., D^{22} 1·077; ethyldipropyl, b. p. 145°/20 mm., D^{22} 1·025. G. F. M.

The Mechanism of the Action of Tribasic Sodium Phosphate on the α-Monochlorohydrin of Glycerol. O. BAILLY (*Compt. rend.*, 1915, **161**, 677—680).—A critical investigation of the interaction of trisodium phosphate and glycerol monochlorohydrin in which

the author shows that the changes are not so simple as that stated by King and Pyman (T., 1914, **105**, 1238):

$$(1)\ Na_3PO_4 + CH_2Cl\cdot CH(OH)\cdot CH_2\cdot OH = NaCl + PO_4Na_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH.$$

The two substances were mixed in equimolecular proportions, the mixture being kept at 18°, and at definite intervals determinations were made of the sodium chloride formed, of the trisodium phosphate destroyed, and of the glycerophosphate formed. The results show that, whilst the sodium chloride formed and the trisodium phosphate destroyed are in molecular agreement throughout, the amount of sodium glycerophosphate formed is always much less than that required by equation (1), the difference being very marked for the first ten hours. The author considers that the formation of sodium glycerophosphate takes place according to equations (2) and (3):

$$(2)\ Na_3PO_4 + CH_2Cl\cdot CH(OH)\cdot CH_2\cdot OH = Na_2HPO_4 + NaCl + \overbrace{CH_2\cdot CH}^{O}\cdot CH_2\cdot OH$$

$$(3)\ \overbrace{CH_2\cdot CH}^{O}\cdot CH_2\cdot OH + Na_2HPO_4 = PO_4Na_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$$

since he has shown that the glycide and disodium hydrogen phosphate do react slowly to give sodium glycerophosphate, about 80% of the glycide being transformed into glycerophosphate in about eight days. W. G.

Electrolysis of the Alkali Salts of Aliphatic Sulphocarboxylic Acids. FR. FICHTER and THEODOR LICHTENHAHN (*Ber.*, 1915, **48**, 1949—1963).—The anodic oxidation of sulphoacetic acid, and its potassium and ammonium salts, of potassium sulphopropionate and ammonium sulphopropionate dissolved in the free acid, of potassium methanesulphonate, and of methanedisulphonic acid and its salts has been investigated.

In the case of sulphoacetic acid and its salts the chief products are sulphuric acid and carbon dioxide, but carbon monoxide, ethylene, formaldehyde, sulphur dioxide, and methane- and ethane-disulphonic acids may be detected, the latter as their barium salts. The normal product, analogous to the electro-synthesis of ethylene, is ethanedisulphonic acid, thus:

$$2SO_3H\cdot CH_2\cdot CO_2H + O = C_2H_4(SO_3H)_2 + 2CO_2 + H_2O.$$

Just after the commencement of the electrolysis, however, the neutral solution becomes alkaline, and later on it accumulates neutral sulphates, conditions which are favourable to the Hofer and Moest reaction (A., 1902, i, 736), in which hydroxyl ions convert the fission product of electrolysis into an alcohol. That is, the residues, $\cdot CH_2\cdot SO_3H$, not only coalesce to form ethanedisulphonic acid, but they give methanolsulphonic acid, $OH\cdot CH_2\cdot SO_3H$. This, of course, is speedily oxidised to the aldehyde, $CHO\cdot SO_3H$, which will give sulphuric acid and formaldehyde on hydrolysis (and therefore also sulphur dioxide and carbon monoxide) or be oxidised to sulphoformic acid, $CO_2H\cdot SO_3H$, and finally to sulphuric acid and

carbon dioxide. The production of ethylene and methanedisulphonic acid is attributed to another reaction of the $\cdot CH_2\cdot SO_3H$ residue, thus: $4\cdot CH_2\cdot SO_3H = 2CH_2(SO_3H)_2 + C_2H_4$.

Just as the production of butane from a propionate falls very much behind the electrosynthesis of ethane, the chief gaseous product being ethylene, so the main result of the electrolysis of a sulphopropionate is the formation of sulphuric acid, ethylene, and carbon dioxide, thus: $SO_3H\cdot CH_2\cdot CH_2\cdot CO_2H + O = H_2SO_4 + C_2H_4 + CO_2$. Here, again, secondary reactions take place, and carbon monoxide, formaldehyde, sulphur dioxide, and acetic acid may be detected among the products.

The electrolysis of potassium methanesulphonate leads to the production of carbon dioxide, the sulphate and a little persulphate, and also formaldehydesulphonic acid, which becomes obvious on boiling the solution. No carbon monoxide or hydrocarbon is formed. The result is an oxidation unaccompanied by synthetic processes, thus: $CH_3\cdot SO_3H + 4O = CO_2 + H_2SO_4 + H_2O$ and

$$CH_3\cdot SO_3H + 2O = CHO\cdot SO_3H + H_2O.$$

Similarly, methanedisulphonic acid or its salts is merely oxidised to sulphuric acid and carbon dioxide, just as it is by 30% hydrogen peroxide.

In the course of the experiments it was observed that barium methanedisulphonate crystallises, not only in the well-known form of very thin, rhombic tablets, but in very characteristic, centimetre-long, transparent needles, arranged in concentric groups. This form is obtained by crystallisation from dilute solutions at a low temperature in the presence of a trace of acid (for example, a drop of 2*N*-HCl). The needles belong to the same system as the tablets.

For the details of the current densities employed and the methods for identifying and isolating the products the original should be consulted. J. C. W.

Trichloro-*tert.*-butyl Acetate (Acetylchloretone). T. B. ALDRICH (*J. Amer. Chem. Soc.*, 1915, **37**, 2720—2723).—When β-trichloropropan-β-ol, $CCl_3\cdot CMe_2\cdot OH$, is heated with a mixture of acetic anhydride and sodium acetate, it is converted into the corresponding *acetate*, $CCl_3\cdot CMe_2\cdot OAc$, b. p. 145—146°/246 mm. Hydrolysis is effected only slowly with water or dilute acids, but concentrated nitric acid causes rapid hydrolysis. The acetate has anæsthetic properties similar to those of the parent alcohol, but its toxicity towards guinea-pigs is slightly less. D. F. T.

Fatty Acid Esters of Ethylene Glycol. R. F. RUTTAN and J. R. ROEBUCK (*Trans. Roy. Soc. Canada*, 1915, **9**, 1—11).—The authors have prepared a number of mono- and di-acid esters from ethylene glycol by direct esterification at high temperatures and with constant stirring. About 30 grams of the acid were mixed with an amount of glycol more than sufficient to convert the whole of the acid into mono-ester, and the mixture was heated at 185—187° in an open flask, being constantly stirred by a platinum stirrer. The mixture after fusion was freed from glycol by washing with hot

water and from free acid by neutralisation with calcium hydroxide. The mono- and di-acid esters were separated by crystallisation from hot alcohol, the di-acid ester separating out first.

Ethylene distearate, $C_2H_4(C_{18}H_{35}O_2)_2$, crystallises in pearly plates, m. p. 75°, n_D^{75} 1·4385, D^{78} 0·8581; 100 grams of alcohol dissolve 0·010 gram at 0°, 0·028 gram at 25°, 0·037 gram at 28°, and 0·112 gram at 40° (compare Würtz, *Ann., Chim. phys.*, 1859, [iii], **55**, 436). The *monostearate*, $C_2H_4(OH)(C_{18}H_{35}O_2)$, crystallises in pearly plates, m. p. 58·5°, $n_D^{58\cdot5}$ 1·4310, D^{60} 0·8780; 100 grams of alcohol dissolve 0·64 gram at 0°, 1·31 grams at 7·4°, 2·10 grams at 16°, 4·17 grams at 25°, 10·61 grams at 29°.

Ethylene dipalmitate, $C_2H_4(C_{16}H_{31}O_2)_2$, crystallises in pearly plates, m. p. 68·7°, $n_D^{68\cdot7}$ 1·4378, $D^{77\cdot9}$ 0·8594; 100 grams of alcohol dissolve 0·018 gram at 0°, 0·087 gram at 25°, 0·109 gram at 29°, 0·31 gram at 38°. The *monopalmitate*, $C_2H_4(OH)(C_{16}H_{31}O_2)$, crystallises in pearly plates, m. p. 51·5°, $n_D^{51\cdot5}$ 1·4411, $D^{60\cdot5}$ 0·8786; 100 grams of alcohol dissolve 1·62 grams at 0°, 5·76 grams at 7·4°, 10·67 grams at 16°, 24·08 grams at 25°.

Ethylene dimargarate, $C_2H_4(C_{17}H_{33}O_2)_2$, crystallises in needles or waxy scales, m. p. 65·5°, n_D^{67} 1·4392, $D^{67\cdot1}$ 0·8605; 100 grams of alcohol dissolve 0·024 gram at 0°, 0·101 gram at 25°. The *monomargarate*, $C_2H_4(OH)(C_{17}H_{33}O_2)$, crystallises in thin plates, m. p. 50·2°, n_D^{52} 1·4440; 100 grams of alcohol dissolve 1·72 grams at 0°.

The esters with oleic acid were not satisfactorily separated as their solidification points seemed very near each other and that of oleic acid itself.

Ethylene chlorohydrin, when heated in a sealed tube for twenty hours at 105—115° with equivalent quantities of either stearic or palmitic acid, gave the corresponding chloroethyl ester, the action ceasing when 18—20% of the acid remained uncombined.

Chloroethyl stearate, $C_2H_4Cl\cdot C_{18}H_{35}O_2$, crystallises in waxy scales, m. p. 48·5°, $D^{49\cdot5}$ 0·9049, $n_D^{48\cdot5}$ 1·4433; 100 grams of alcohol dissolve 0·20 gram at 0°, 0·28 gram at 7·4°, 1·29 grams at 16°, 2·10 grams at 25°, 3·62 grams at 29°.

Chloroethyl palmitate, $C_2H_4Cl\cdot C_{16}H_{31}O_2$, crystallises in pearly plates, m. p. 41·5°, $n_D^{41\cdot5}$ 1·445, $D^{46\cdot1}$ 0·9097; 100 grams of alcohol dissolve 0·48 gram at 0°, 1·16 grams at 7·4°, 3·8 grams at 16°, 8·87 grams at 25°, 15·31 grams at 29°.

Chloroethyl stearate, when heated with the calculated quantity of silver palmitate at 140° for three to four hours, or with potassium palmitate for a much longer time, gives *ethylene, stearopalmitate*, $C_2H_4(C_{18}H_{35}O_2)(C_{16}H_{31}O_2)$, m. p. 65°, n_D^{65} 1·4391, $D^{70\cdot5}$ 0·8584; 100 grams of alcohol dissolve 0·011 gram at 0°, 0·035 gram at 25°, 0·049 gram at 29°, 0·213 gram at 39°. W. G.

Catalytic Bleaching of Palm Oil. SOSALE GARALAPURY SASTRY (T., 1915, **107**, 1828—1831. Compare *Eng. Pat.*, 17784 of 1913).—A series of experiments is described on the bleaching of palm oil by blowing air or oxygen through it, both air and oil being at 80—90°, in the presence of the salts and oxides of manganese, cobalt, nickel, iron, and lead. Manganese borate, and particularly cobalt borate,

are found to be very efficient catalysts for this purpose, for 60—70 grams of a crude oil were completely bleached in the presence of 0·01% of the latter by a current of air flowing at the rate of about 17 litres per hour for three and a-half hours. The bleaching was permanent, and oils treated in this way retain their characteristic perfume and soap-making qualities. J. C. W.

Preparation of a [Cobalt] Salt of Cholic Acid. KNOLL & Co. (D.R.-P. 284762; from *J. Soc. Chem. Ind.*, 1915, **34**, 1166).—*Cobalt cholate*, $[C_{24}H_{35}O_9]_2Co$, is prepared by the interaction of an alkali cholate with a cobalt salt, or by other common methods. It readily swells in water, but dissolves sparingly in water and alcohol and not at all in ether, benzene, or chloroform. It has disinfecting properties when taken internally, but therapeutic doses do not injure the mucous membrane of the stomach. J. C. W.

Magnesium Citrate in Aqueous Solution. FRANCINE SWART and C. BLOMBERG (*J. Pharm. Chim.*, 1915, [vii], **12**, 387—391).—The authors do not agree with the existence of a heptahydrate of magnesium citrate as described by Léger (A., 1915, i, 496). They explain the slow separation of magnesium citrate tridecahydrate from aqueous solution as due to the ionisation of the citrate giving rise to two complex ions (compare A., 1915, ii, 737), which slowly recombine to form the molecule, which then crystallises as the tridecahydrate. They reaffirm the existence of the basic magnesium citrate, $Mg_2\overline{Ci}\cdot OH$, previously described by Blomberg (*Pharm. Weekblad.*, 1915, September), and explain its formation by means of these complex ions. W. G.

Magnesium Citrate in Aqueous Solution. E. LÉGER (*J. Pharm. Chim.*, 1915, [vii], **12**, 391—394).—A reply to Swart and Blomberg (preceding abstract). W. G.

Bromoacetylxylose and β-Triacetylmethylxyloside. J. K. DALE (*J. Amer. Chem. Soc.*, 1915, **37**, 2745—2747).—By treating xylose with a saturated solution of hydrobromic acid in acetic anhydride at the ordinary temperature, *bromotriacetylxylose*, crystals, m. p. 102°, $[\alpha]_D^{20}$ +212·2° (in chloroform), can be produced. This substance in acetic acid solution reacts with silver acetate, giving *β-tetra-acetylxylose* (compare Hudson and Johnson, following abstract), and when treated in methyl alcohol with silver nitrate yields *β-triacetylmethylxyloside*, thin, plate-like crystals, m. p. 115°, $[\alpha]_D^{20}$ −60·5°, which is converted by cold dilute sodium hydroxide solution into β-methylxyloside (Fischer, A., 1895, i, 439). D. F. T.

The Isomeric Tetra-acetates of Xylose. The Acetates of Melibiose, Trehalose, and Sucrose. C. S. HUDSON and J. M. JOHNSON (*J. Amer. Chem. Soc.*, 1915, **37**, 2748—2753).—Tetra-acetylxylose, m. p. 128° (corr.) (Stone, A., 1894, i, 104; Bader, A., 1896, i, 336) when heated in acetic anhydride containing a little

zinc chloride undergoes chemical change, as is clear from the occurrence of a marked increase in the optical activity of the solution, and there can be separated from the solution an *isomeride*, m. p. 59° (corr.); an unstable *alcoholate* of this substance was isolated as an intermediate product in the process of separation. The optical activity of the new compound is $[\alpha]_D^{20}$ +88·9° in chloroform, +80·4° in benzene, and +95·8° in acetic acid, whereas for the original compound, m. p. 128°, the values for solutions of approximately the same concentration (approx. 10%) were $[\alpha]_D^{20}$ −25·1°, −22·3°, and −7·3° respectively in the same three solvents; the former compound is therefore termed α-tetra-acetylxylose as a probable derivative of the known dextrorotatory α-xylose, whilst the less fusible lævorotatory compound is termed β-tetra-acetylxylose, from its presumed relationship with the hypothetical β-xylose. On hydrolysis of the α-tetra-acetyl derivative with alcoholic potassium hydroxide at 0°, only ordinary xylose was obtained, but acetylation of xylose with a mixture of acetic anhydride and commercial pyridine (compare Behrend, A., 1907, i, 481) gave a mixture of the α- and β-forms of the tetra-acetyl compound. The tetra-acetylxylose obtained by Ryan and Ebrill (A., 1908, i, 716) by the action of silver acetate on chloroacetoxylose in acetic acid is shown to be the β-isomeride, and an improved method is given for the preparation of chloroacetoxylose, consisting in boiling xylose with acetyl chloride and a trace of zinc chloride until the sugar is completely dissolved. An acetic acid solution of hydrogen bromide rapidly converted both the α- and the β-tetra-acetyl compounds into one and the same bromoacetoxylose (compare Dale, preceding abstract), which was converted by methyl alcohol and silver nitrate into β-triacetylmethylxyloside.

Melibiose octa-acetate, m. p. 177·5° (corr.), $[\alpha]_D$ +102·5° and +101·9° in chloroform and acetic acid respectively, when heated at 100° in acetic anhydride containing a little zinc chloride, undergoes a marked increase in optical activity, presumably due to the formation of an *isomeride*, but the latter could only be isolated as a syrup. The new and more active isomeride will be the α-form, whilst the original compound is to be represented as the β-isomeride.

Trehalose octa-acetate, m. p. 96—98°, $[\alpha]_D^{20}$ +162·3° in chloroform, and sucrose octa-acetate, m. p. 69°, $[\alpha]_D^{20}$ +59·6° in chloroform, showed no alteration in optical activity when dissolved in acetic anhydride with a little zinc chloride, thus indicating the non-existence of isomerides, as would indeed be expected from the lack of muta-rotation and the non-aldehydic character of these sugars.

D. F. T.

A Second Crystalline Lævulose Penta-acetate (α-Lævulose Penta-acetate). C. S. HUDSON and D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1915, **37**, 2736—2745).—By the action of zinc chloride in acetic anhydride solution on lævulose tetra-acetate the authors have obtained a *d*-lævulose penta-acetate, m. p. 70°, $[\alpha]_D^{20}$ +34·75° (in chloroform), and therefore quite distinct from the isomeric penta-acetate, m. p. 108°, $[\alpha]_D^{20}$ −120·9°, recently described by the authors

(A., 1915, i, 502). This new penta-acetate shows the same stability as that earlier described towards zinc chloride, and therefore the method applicable to the establishment of equilibrium between aldose acetates fails in this case of a ketose derivative. The penta-acetate, m. p. 108°, is obtained when lævulose tetra-acetate is treated in the cold with sulphuric acid and acetic anhydride, so that the same cyclic system must be present in both the penta-acetates, which are therefore designated by the terms α- and β- for the more fusible and the less fusible isomerides respectively. α-Lævulose penta-acetate can also be obtained directly from lævulose by the action of zinc chloride in acetic anhydride solution and by the action of pyridine in the same solvent, but the process described above is the most satisfactory.

The best method for the production of lævulose tetra-acetate is with an acetic anhydride solution of zinc chloride and lævulose at 0°, stopping the reaction as soon as the last substance has passed into solution. A 30% yield of tetra-acetate can thus be obtained.

β-Lævulose penta-acetate when treated with an acetic acid solution of hydrogen bromide is converted into lævulose tetra-acetate, probably by way of the corresponding bromoacetyl compound. The α-penta-acetate is unaffected by similar treatment, so that it is probably correct to regard the tetra-acetate as a β-compound.

As the original crystalline lævulose was a β-compound, and as the α- and β-penta-acetates do not give an equilibrium mixture, it is probable that in the production of the former from lævulose a molecular rearrangement occurs in one of the less acetylated derivatives, but no experimental indication was forthcoming as to the stage of the acetylation at which rearrangement occurs.

The authors have also prepared from lævulose tetra-acetate a crystalline tetra-acetylmethyl-lævuloside, which is to be described later. D. F. T.

Action of Cyanides of the Alkali and the Alkaline Earth Metals on Sugars. II. E. Rupp and A. Hölzle (*Arch. Pharm.*, 1915, **253**, 404—415. Compare A., 1914, i, 142).—The preparation of α-glucoheptoic anhydride from dextrose is effected more conveniently by barium cyanide than by potassium cyanide. The latter causes the formation of dark-coloured by-products, but when its hydrolytic dissociation is diminished, by the use, for example, of potassium zincocyanide, the reaction product is obtained, and remains, nearly colourless. Zinc cyanide or mercuric cyanide has no action on dextrose in aqueous solution.

α-Glucoheptoic anhydride has recently come into use as a diabetic sugar under the name hediosite. *Basic barium glucoheptoate*, $OH\cdot CH_2\cdot[CH\cdot OH]_5\cdot CO\cdot O\cdot Ba\cdot OH$, colourless, crystalline precipitate, is obtained by heating hediosite and barium hydroxide (1 mol.) in saturated aqueous barium hydroxide at 75°. The basic salt, being sparingly soluble, can be utilised to isolate the product of the reaction between dextrose and an alkali cyanide, the yield of hediosite by this method being 30—33%.

The velocity of reaction of a 10% dextrose solution and potassium

cyanide (1 mol.) has been followed polarimetrically, the results being controlled by estimations of the ammonia evolved. About one-half of the sugar has reacted within two hours, and the reaction ceases after three days. The estimation of the cyanide undecomposed shows that the consumption of the cyanide increases rapidly with the concentration of the solution; the amount of potassium cyanide decomposed in a 10% dextrose solution in a few days is about the same as that decomposed in a 0·1% solution after one month. The consumption of the cyanide is enormously accelerated catalytically by alkalis; a solution of dextrose and potassium cyanide, when faintly acidified with sulphuric acid, suffers in the course of weeks no greater loss of cyanide than does the same solution within a few hours after the addition of two drops of dilute sodium hydroxide or a few drops of aqueous ammonia.

Mannose and potassium or barium cyanide react in aqueous solution with the evolution of ammonia and the formation of barium mannosecarboxylate, from which the corresponding lactone is obtained by acidification.

Lævulose and potassium or barium cyanide react, hydrogen cyanide, followed after several hours by ammonia, being evolved; the product obtained by evaporating the solution over sulphuric acid in a vacuum is probably potassium lævulosecarboxylate, but the free acid could not be isolated. The behaviour of galactose is quite similar to that of lævulose. In the case of lactose, hydrogen cyanide is evolved, followed after several days by ammonia. The solution contains a dark-coloured, viscous mass which was not further examined; estimations of the undecomposed cyanide after the lapse of days show that the biose reacts smoothly with 1 mol. of the cyanide, the more rapidly the greater is the concentration of the solution, but subsequently a second molecule of the cyanide is very slowly decomposed. These results are interpreted as indicating the formation of potassium lactosecarboxylate, which is then hydrolysed to potassium glucoheptoate and galactose, the latter being subsequently converted slowly into potassium galactosecarboxylate.

The behaviour of maltose is very similar to that of lactose, except that a second molecule of the cyanide scarcely enters into reaction.

C. S.

Preparation of Melibiose. C. S. HUDSON and T. S. HARDING (*J. Amer. Chem. Soc.*, 1915, **37**, 2734—2736).—By a modification of the method of Bau and Loiseau (A., 1904, i, 225, 475) the authors have been able to prepare melibiose from raffinose with a yield of 175—200 grams of pure crystalline product from 500 grams of the triose.

Pure raffinose (500 grams) obtained by the process of Hudson and Harding (A., 1914, i, 1166) was taken in approximately 10% aqueous solution, together with baker's yeast (10 grams), acetic acid (one or two drops), and malt sprouts (1 gram), the latter serving as a nitrogenous food; after thirty-six to forty-eight hours at the ordinary temperature, the optical activity had fallen to approxi-

mately that calculated for the resulting melibiose, the lævulose having undergone further fermentation to carbon dioxide and alcohol. The solution was then filtered, cleared with basic lead acetate solution, decolorised by carbon, and, after evaporation to a syrup, caused to crystallise by the addition of alcohol and a nucleus of melibiose. D. F. T.

Complex Metallic Ammines. II. Additive Compounds Formed from *trans*-Dichlorodiethylenediaminecobaltic Chloride. THOMAS SLATER PRICE and SIDNEY ALBERT BRAZIER (T., 1915, **107**, 1713—1740).—The formation of the additive compound between *trans*-dichlorodiethylenediaminecobaltic chloride and thiodiacetic acid (A., 1915, i, 942) has led to the investigation of other dibasic acids, including not only those containing sulphur, but also acids of the oxalic acid series and certain unsaturated dibasic acids. It was found that all dibasic acids do not give rise to additive compounds; with one or two exceptions the compounds formed are of two types, which may be formulated as $[Cl_2Co\,en_2]AH,H_2A$ and $[Cl_2Co\,en_2]AH$, where H_2A is a dibasic acid. Acids which give compounds of the first type are: malonic, chloromalonic, bromomalonic, glutaric, acetonedicarboxylic, thiodiacetic, sulphonyldiacetic, and maleic acids, whilst the following acids give compounds of the second type: oxalic, methylmalonic, ethylmalonic, dimethylmalonic, diethylmalonic, dichloromalonic, dibromomalonic, succinic, dibromosuccinic, tartaric, *meso*-tartaric, adipic, dithiodiacetic, dithiodipropionic, fumaric, citraconic, mesaconic, and itaconic acids. Thiodipropionic acid gives a compound of the type

$$[Cl_2Co\,en_2]Cl,H_2A.$$

A detailed consideration of the results hitherto obtained by Werner in connexion with analogous compounds, together with the above results, leads the authors to the conclusion that the additive compounds should be formulated as $A{<}\begin{matrix}H\cdots\\ H\cdots\end{matrix}\left[\begin{matrix}\cdots Cl\\ \cdots Cl\end{matrix}\;Co\;en_2\right]AH$, the hydrogens of the acid being connected with the chlorines of the complex by subsidiary valencies. An explanation of the fact that only certain dibasic acids give additive compounds is given in the light of the results hitherto obtained by Böeseken (A., 1913, i, 1147) and Irvine and Steel (A., 1915, ii, 669), it being shown that in all probability the acids giving rise to compounds of the first type have their hydroxyl groups in the *cis*-position with respect to each other, malonic acid, for example, having the configuration $\begin{array}{l}CO\cdot CH_2\cdot CO\\ |\qquad\quad\;\; |\\ OH\qquad\; OH\end{array}$; the hydroxyl groups are then in a favourable position for their hydrogen atoms to combine with the chlorine atoms of the dichloro-compound. Of the acids giving compounds of the second type, it is shown that all of them, with the exception of the substituted malonic acids and citraconic acid, probably have their hydroxyl groups in the *anti*-position with respect to each other, that is, not in a favourable position for their hydrogen atoms to combine with the chlorine atoms of the dichloro-compound. The fact that certain substituted malonic acids, together with citraconic

acid, do not give additive compounds, although their hydroxyl groups are probably in the *cis*-position with respect to each other, is explained on the assumption that the substitution of hydrogen by radicles with much larger molecular volumes, as, for example, methyl, ethyl, and the halogens, influences the relative positions in space of the hydroxyl groups in such a manner that they are not favourably situated for forming an additive compound.

In order to prepare the various compounds, cold concentrated solutions of *trans*-dichlorodiethylenediaminecobaltic chloride and the acid were mixed, the proportions taken being one molecular equivalent of the chloride to rather more than two molecular equivalents of the acid. If no precipitate was formed, sufficient sodium carbonate to form the sodium hydrogen salt of the acid was added, when precipitation rapidly took place. When the acid forms an additive compound it is immaterial whether it be present in the reaction mixture as the free acid or the sodium hydrogen salt. All the compounds thus obtained were micro-crystalline. The fresh aqueous solutions do not contain ionic chlorine, but on keeping they slowly change in colour, probably with the formation of chloroaquo-compounds.

trans-*Dichlorodiethylenediaminecobaltic hydrogen oxalate*, $YC_2O_4H,2H_2O$, where $Y=[Cl_2Co\,en_2]$, forms emerald-green, striated, and elongated plates. In one case, under conditions which have to be investigated further, the *trans*-dichloro-chloride and ammonium hydrogen oxalate gave crystals of *oxalic acid*-trans-*dichlorodiethylenediaminecobaltic hydrogen oxalate*, $YC_2O_4H,C_2H_2O_4$. From the hydrogen oxalate, oxalatodiethylenediaminecobaltic chloride, $[C_2O_4Co\,en_2]Cl,4H_2O$, is readily obtained by boiling the solution and subsequent concentration. *Malonic acid*-trans-*dichlorodiethylenediaminecobaltic hydrogen malonate*,

$$YC_3O_4H_3,CH_2(CO_2H)_2,2H_2O,$$

forms dark, emerald-green, blunt prisms; when the dichloro-chloride and the malonic acid were in the proportions of 2:1 by weight, instead of 3:4, as in preparing the above compound, *malonic acid*-trans-*dichlorodiethylenediaminecobaltic chloride*, $YCl,CH_2(CO_2H)_2$, was obtained. trans-*Dichlorodiethylenediaminecobaltic hydrogen diethylmalonate*, $YCO_2\cdot CEt_2\cdot CO_2H$, crystallises as emerald-green, square plates, mixed with a few needles; the corresponding *hydrogen dimethylmalonate*, $YCO_2\cdot CMe_2\cdot CO_2H$, gives nodular aggregates of dark, emerald-green crystals. The *hydrogen ethylmalonate*, $YCO_2\cdot CHEt\cdot CO_2H$, and the *hydrogen methylmalonate*, $YCO_2\cdot CHMe\cdot CO_2H$, each form emerald-green, blunt-ended prisms. trans-*Dichlorodiethylenediaminecobaltic hydrogen dibromomalonate*, $YCO_2\cdot CBr_2\cdot CO_2H$, consists of apple-green, blunt-ended, prismatic crystals; the aqueous solution loses carbon dioxide on the water-bath, and on evaporation *dibromoacetic acid*-trans-*dichlorodiethylenediaminecobaltic dibromoacetate*, $YC_2HO_2Br_2,CHBr_2\cdot CO_2H$, is obtained in the form of milky, green, irregular plates.

Bromomalonic acid-trans-*dichlorodiethylenediaminecobaltic hydrogen bromomalonate*, $YCO_2\cdot CHBr\cdot CO_2H,CHBr(CO_2H)_2$, crystallises in emerald-green plates; the corresponding *chloromalonate*,

$YCO_2\cdot CHCl\cdot CO_2H,CHCl(CO_2H)_2$, also gives emerald-green crystals. Each of these compounds, when thoroughly washed with alcohol, loses a molecule of the halogenomalonic acid, giving respectively trans-*dichlorodiethylenediaminecobaltic hydrogen bromomalonate*, $YCO_2\cdot CHBr\cdot CO_2H$, and the corresponding trans-*hydrogen chloromalonate*, $YCO_2\cdot CHCl\cdot CO_2H$. trans-*Dichlorodiethylenediaminecobaltic hydrogen dichloromalonate*, $YCO_2\cdot CCl_2\cdot CO_2H$, crystallises as a conglomerate of light, emerald-green plates; the aqueous solution loses carbon dioxide on the water-bath, and on evaporation emerald-green crystals of *dichloroacetic acid*-trans-*dichlorodiethylenediaminecobaltic dichloroacetate*, $YC_2HO_2Cl_2,CHCl_2\cdot CO_2H$, are obtained. Under similar conditions the additive compound with chloromalonic acid gives emerald-green, flat prisms of *chloroacetic acid*-trans-*dichlorodiethylenediaminecobaltic chloroacetate*,

$$YC_2H_2O_2Cl,CH_2Cl\cdot CO_2H,$$

although the pure compound is best obtained from chloroacetic acid and the *trans*-dichloro-chloride.

trans-*Dichlorodiethylenediaminecobaltic hydrogen succinate*, $YCO_2\cdot[CH_2]_2\cdot CO_2H,H_2O$, crystallises in dark, emerald-green, blunt-ended prisms. The *hydrogen dibromosuccinate*,

$$YCO_2\cdot[CHBr]_2\cdot CO_2H,$$

gives malachite-green crystals of indefinite shape. The *hydrogen tartrate*, $YCO_2\cdot[CH\cdot OH]_2\cdot CO_2H,H_2O$, and *hydrogen* meso*tartrate*, $YCO_2\cdot[CH\cdot OH]_2\cdot CO_2H$, crystallise as a felted mass of emerald-green needles, and as an emerald-green conglomerate of very small plates (?) respectively. The *hydrogen adipate*,

$$YCO_2\cdot[CH_2]_4\cdot CO_2H,$$

gives dark, emerald-green, square plates, as also does the *hydrogen dithiodiacetate*, $YCO_2\cdot CH_2\cdot S_2\cdot CH_2\cdot CO_2H,H_2O$. The *hydrogen dithiodipropionate*, $YCO_2\cdot CHMe\cdot S_2\cdot CHMe\cdot CO_2H,H_2O$, gives pale, emerald-green crystals, whilst the *hydrogen fumarate*,

$$YCO_2\cdot CH\colon CH\cdot CO_2H,$$

gives irregular plates of the same colour. The *hydrogen citraconate*, *hydrogen mesaconate*, and *hydrogen itaconate*, $YC_5H_5O_4$, form respectively emerald-green crystals, pale green plates, and emerald-green needles.

Glutaric acid-trans-*dichlorodiethylenediaminecobaltic hydrogen glutarate*, $YCO_2\cdot[CH_2]_3\cdot CO_2H,[CH_2]_3(CO_2H)_2$, gives dark, emerald-green, elongated plates. The following are also additive compounds: *hydrogen thiodiacetate*, $YCO_2\cdot CH_2\cdot S\cdot CH_2\cdot CO_2H,S(CH_2\cdot CO_2H)_2$, emerald-green plates; *hydrogen sulphonyldiacetate*,

$$YCO_2\cdot CH_2\cdot SO_2\cdot CH_2\cdot CO_2H,SO_2(CH_2\cdot CO_2H)_2,$$

very small, emerald-green plates; hydrogen maleate,

$$YC_4H_3O_4,C_4H_4O_4,$$

emerald-green needles. *Thiodiacetic acid*-trans-*dibromodiethylenediaminecobaltic hydrogen thiodiacetate*,

$$[Br_2Co\,en_2]CO_2\cdot CH_2\cdot S\cdot CH_2\cdot CO_2H,S(CH_2\cdot CO_2H)_2,$$

forms pea-green crystals, whilst *thiodipropionic acid*-trans-*dichlorodiethylenediaminecobaltic chloride*, $YCl,S(CHMe\cdot CO_2H)_2$, crystallises in dark, grass-green plates.

The following *cis*-isomerides were also obtained: cis-*dichlorodi-*

ethylenediaminecobaltic oxalate, $Y_2C_2O_4$, violet crystals; cis-*hydrogen succinate*, $YCO_2 \cdot (CH_2)_2 \cdot CO_2H$, violet, short, blunt-ended prisms; and cis-*adipate*, $Y_2(CO_2)_2(CH_2)_4$, violet prisms, with blunt ends.

A pure substance was not isolated from acetonedicarboxylic acid, but the results indicated the formation of an additive compound.

A solution of the additive compound formed with thiodiacetic acid, when treated with potassium iodide, gave a vivid green precipitate, consisting of a conglomerate of very small, tabular crystals of trans-*dichlorodiethylenediaminecobaltic iodide*, YI. T. S. P.

A New Oxidation Method. III. Action of Aldehydes on Primary Hydroxy amines. K. Hess and Cl. Uibrig (*Ber.*, 1915, **48**, 1974—1985. Compare A., 1914, i, 199).—The behaviour of hydroxylated primary amines towards formaldehyde, acetaldehyde, and benzaldehyde has been investigated.

When diacetonalkamine is treated with formaldehyde in the cold, it first condenses according to the scheme:

$$NH_2 \cdot CMe_2 \cdot CH_2 \cdot CHMe \cdot OH + CH_2O \rightleftharpoons OH \cdot CH_2 \cdot NH \cdot CMe_2 \cdot CH_2 \cdot CHMe \cdot OH.$$

At about 50°, however, the product is an anhydride of the latter compound, namely, *methylenediacetonalkamine* [*β-methyleneamino-β-methylpentan-δ-ol*], $CH_2{:}N \cdot CMe_2 \cdot CH_2 \cdot CHMe \cdot OH$, which is a very pale yellow oil, b. p. 45—47°/23 mm., 150—155°/720 mm., and forms a *picrate*, $C_{13}H_{18}O_8N_4$, long, stout spikes, m. p. 138—139°. In the earlier paper this was mistaken for the isomeric diacetonmethylamine, $NHMe \cdot CMe_2 \cdot CH_2 \cdot COMe$, but it cannot be that, for it is formed too easily and is too easily hydrolysed. At higher temperatures further reactions take place. Thus, when diacetonalkamine was heated with 40% formaldehyde at 142—145° in a sealed tube and the product was extracted with ether and then fractionated, the following were isolated: the above methylenediacetonalkamine, then *diacetondimethylamine* [*β-dimethylamino-β-methylpentan-δ-one*], $NMe_2 \cdot CMe_2 \cdot CH_2 \cdot COMe$, b. p. 59—61°/23 mm., a limpid, mobile, highly refractive oil with a strong narcotic odour (*picrate*, m. p. 183°), and finally methyldiacetonalkamine, $NHMe \cdot CMe_2 \cdot CH_2 \cdot CHMe \cdot OH$, b. p. 73—75°/20 mm.

The chief product obtained by heating diacetonalkamine with 40% acetaldehyde acidified with hydrochloric acid at 115—120° was *ethylenediacetonalkamine* [*β-ethyleneamino-β-methylpentan-δ-ol*], $C_8H_{17}ON$, a colourless, mobile oil, b. p. 42—47°/12 mm., with a powerful narcotic odour (*picrate*, stout needles, m. p. about 147°). Similarly, benzaldehyde yields *benzylidenediacetonalkamine* [*β-benzylideneamino-β-methylpentan-δ-ol*],

$$CHPh{:}N \cdot CMe_2 \cdot CH_2 \cdot CHMe \cdot OH,$$

a yellow oil, b. p. 94—95°/0·1 mm., 139—140°/19 mm., with a faint basic odour (*picrate*, long, prismatic needles, m. p. 170—171°). The base is quickly transformed into the *hydrochloride*, pink, m. p. 199°, when covered with concentrated hydrochloric acid, and it is readily hydrolysed, even in water.

The *urethane* of diacetonalkamine [*β-carbethoxyamino-β-methylpentan-δ-ol*], $CO_2Et \cdot NH \cdot CMe_2 \cdot CH_2 \cdot CHMe \cdot OH$, was prepared as a

viscous oil, b. p. 142°/23 mm., by the agency of ethyl chloroformate. When this is heated with an excess of 40% formaldehyde at 145—150° it forms *β-carbethoxymethylamino-β-methylpentan-δ-one*, $CO_2Et·NMe·CMe_2·CH_2·COMe$, b. p. 123—125°/14 mm., which readily yields formaldehyde again in the presence of water. If the urethane is mixed with alcohol and formaldehyde and heated at 200°, however, it yields the methylene *compound*,

$$(OH·CHMe·CH_2·CMe_2·NH)_2CH_2,$$

which crystallises in the triclinic system, and has m. p. 132°, b. p. 165—170°/25 mm.

Aminoethyl alcohol was shaken with propyl chloroformate and sodium carbonate solution and converted into *β-carbopropoxyamino-ethyl alcohol*, $CO_2Pr·NH·CH_2·CH_2·OH$, a viscous oil, b. p. 150—151°/13 mm. When this is heated with 40% formaldehyde at 145° it yields *carbopropoxymethylaminoacetaldehyde*,

$$CO_2Pr·NMe·CH_2·CHO,$$

a highly refractive, limpid, pleasant-smelling oil, b. p. 103—105°/13 mm., which reduces ammoniacal silver oxide and forms a hydrazone.

β-Amino-α-phenylethyl alcohol, obtained by reducing benzaldehyde cyanohydrin by sodium amalgam, was also converted into the *urethane* [*β-carbethoxyamino-α-phenylethyl alcohol*],

$$OH·CHPh·CH_2·NH·CO_2Et,$$

pearly leaflets, m. p. 86°, by the agency of ethyl chloroformate. When this is heated with excess of formaldehyde at 140—145° it yields *phenyl carbethoxymethylaminomethyl ketone*,

$$COPh·CH_2·NMe·CO_2Et,$$

b. p. 181—183°/16 mm. J. C. W.

Behaviour of Amino-acids towards Neutral Salts in Aqueous Solution. P. PFEIFFER [with J. WÜRGLER and FR. WITTKA] (*Ber.*, 1915, **48**, 1938—1943. Compare A., 1915, i, 868).—In connexion with physiological processes it is important to determine whether the complex "neutral-salt compounds" of the amino-acids and polypeptides with salts of the alkali and alkaline earth metals can exist as such, in equilibrium with their components and complex ions, in aqueous solutions. This has been tested by determining the solubilities of various amino-acids in salt solutions, by observing the influence of salts on the rotation of *d*- and *l*-alanine in aqueous solution, and by measuring the depression of the freezing point of water containing glycine and various salts. In all cases in which "neutral-salt compounds" are known to exist in the solid state, the solubility of the amino-acid in the particular salt solution is much increased. The rotation of alanine is raised as much as six times by certain salts, just as it is by mineral acids. The depression of the freezing point of water caused by glycine + a salt is less than the sum of the depressions caused by the separate solutes. It seems, therefore, that the complex molecules do exist in aqueous solution. J. C. W.

Preparation of Compounds of Urethanes and Diurethanes with Metallic Bromides. GEHE & CO. (D.R.-P., 284734; from

J. Soc. Chem. Ind., 1915, **34**, 1166).—Urethanes (4 mols.) are heated with calcium or strontium bromide (1 mol.) in a suitable solvent for several hours. The products, especially the double *compound* of calcium bromide with ethyl carbamate,

$$CaBr_2,4NH_2\cdot CO_2Et,$$

are powerful hypnotics, and are useful in the treatment of nocturnal epilepsy; they have no deleterious action on the heart or respiration. J. C. W.

Preparation of Carbamide Nitrate from Cyanamide. OESTERREICHISCHER VEREIN FÜR CHEM. UND METALL. PRODUKTION (D.R.-P. 285259; from *J. Soc. Chem. Ind.*, 1915, **34**, 1166).—Carbamide nitrate is precipitated almost quantitatively when concentrated solutions of cyanamide and nitric acid are mixed at below 20°, thus: $CN\cdot NH_2 + HNO_3 + H_2O = CO(NH_2)_2,HNO_3$. J. C. W.

Reaction of Nitroprusside with Thiocarbamide. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 434—441. Compare A., 1913, i, 606; 1914, i, 967).—The author has investigated the reddish-violet salt obtained by Hofmann (A., 1900, i, 591) by the action of sodium nitroprusside on thiocarbamide, and regarded by him as having the formula $[Fe(CN)_5NO\cdot S\cdot C(NH)\cdot NH_2]Na_3$. That this formula is erroneous is shown by the analytical results, which give 1 : 7, and not 1 : 8, for the ratio, Fe : N; in correspondence with this fact is the author's observation that the synthesis of the compound is accompanied by the liberation of nitrogen. It is known also that, in presence of a weak acid, alkali nitrites transform thiocarbamide into thiocyanic acid with quantitative evolution of nitrogen (compare Werner, T., 1912, **101**, 2180; Coade and Werner, T., 1913, **103**, 1221), $NH_2\cdot CS\cdot NH_2 \longrightarrow NH_2\cdot CS\cdot OH \longrightarrow HNCS$. The assumption is therefore made that the nitroso-group of the nitroprusside reacts, not with the sulphur atom, but with the amino-groups of the thiocarbamide:

$$2Na_2Fe(CN)_5NO + CS(NH_2)_2 \xrightarrow{NaOH}$$
$$Na_3[Fe''(CN)_5NO\cdot NH\cdot CO\cdot SH] + Na_3[Fe(CN)_5,H_2O] + N_2,$$

the first of these products representing Hofmann's reddish-violet salt. The formation of the aquo-salt (compare Hofmann, *loc. cit.*) in considerable proportion has, indeed, been observed, and the accuracy of this representation of the reaction is indicated by the following results. The interaction of sodium nitroprusside and thiocarbamide in methyl-alcoholic solution in presence of excess of sodium alkyloxide yields an orange-yellow salt, which undoubtedly contains one thiocarbamide residue to two atoms of iron, and has probably the formula,

$$Na_7[Fe''(CN)_5\ldots NO\cdot NH\cdot CO\cdot S\cdot Fe''(CN)_5];$$

in aqueous solution this compound decomposes with formation of Hofmann's salt. Treatment of the latter with sodium hydroxide in aqueous methyl-alcoholic solution yields a deliquescent, brownish-orange-yellow salt of the composition $Na_5[Fe(CN)_5NO\cdot N\cdot CO\cdot S]$; this undergoes immediate hydrolysis to the original salt in aqueous

solution, whilst, when kept for a long time in a vacuum in presence of water it undergoes partial decomposition with liberation of nitrogen dioxide. By silver or mercuric salts in the hot, Hofmann's salt is rapidly decomposed with liberation of nitrogen dioxide in the proportion 1NO : 1Fe; under similar conditions the salt obtained from thiocarbamide in methyl-alcoholic solution liberates nitrogen dioxide in the proportion 0·5NO : 1Fe, in accordance with the formula given above.

Reduction of Hofmann's red salt by means of sodium amalgam gives a yellow salt, $Na_3[Fe''(CN)_5 \cdot NH_2 \cdot NH \cdot CO \cdot SH]$, in which the presence of the hydrazine residue, $NH_2 \cdot NH \cdot$, is demonstrated by the behaviour towards mercuric salts or oxide, silver salts, or Fehling's solution, which cause rapid decomposition with liberation of nitrogen, even in the cold; bromine water also liberates nitrogen, but yields no nitroprusside, whereas, under similar conditions, the red salt gives nitroprusside, but no gas.

Hofmann's formula was based solely on the reaction of the red salt with ferric chloride, which gives a green coloration or precipitate, but the author has observed similar behaviour with ferrocyanides containing nitroso-ketones, these being also intensely coloured. The possibility of the formula

$$Na_3[Fe'''(CN)_5NO \cdot NH \cdot CO \cdot S]$$

for the red salt is discussed; this salt does not, however, exhibit the characters of ferricyanides, whilst the ferrous formula is in accord with its behaviour towards alkalis. T. H. P.

The Hydrazide of Cyanoacetic Acid, Oximinocyanoacetic Acid, and Nitrocyanoacetic Acid. AUGUST DARAPSKY and DIETRICH HILLERS (*J. pr. Chem.*, 1916, [ii], **92**, 297—341).—Methyl cyanoacetate (1 mol.) when heated in alcoholic solution with hydrazine hydrate (2 mols.) was converted into cyanoacetylhydrazide, the *hydrochloride* (crystals, m. p. 145°) of which when treated in aqueous solution with sodium nitrite under a layer of ether was converted into *cyanoacetylazide*, $CN \cdot CH_2 \cdot CO \cdot N_3$, a pale yellow, explosive oil of extremely pungent odour; this substance reacted with aniline in ethereal solution, giving cyanoacetanilide, and with boiling alcohol yielding *cyanomethylurethane*, $CN \cdot CH_2 \cdot NH \cdot CO_2Et$, silky needles or slender prisms, m. p. 145°. When heated with diluted hydrochloric acid, the urethane compound underwent disruption, giving carbon dioxide, alcohol, ammonia, and glycine, aminoacetonitrile probably being formed as an unisolatable intermediate product. The last reaction is of little importance as a method of preparing glycine, but an analogous series of reactions with the alkyl derivatives of ethyl cyanoacetate may prove useful for the preparation of other amino-acids. It is of interest that the above method for the preparation of glycine from chloroacetic acid through cyanoacetic acid gives a product in which the amino-group and the carboxyl groups are held by different valencies from those occupied by the same groups in the product prepared by the action of ammonia on chloroacetic acid. These two modes for the preparation of glycine can therefore serve as the basis of a proof of the

equivalence of the four bonds of the carbon atom, by applying them to ordinary chloroacetic acid and to chloroacetic acid prepared by the stages: $CH_2Cl{\cdot}CO_2H \longrightarrow CN{\cdot}CH_2{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH_2{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CHCl{\cdot}CO_2H \longrightarrow CH_2Cl{\cdot}CO_2H$, and $CH_2Cl{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH_2{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CHCl{\cdot}CO_2H \longrightarrow$

$$CO_2H{\cdot}CH(CO_2H){\cdot}CO_2H \longrightarrow$$

$CO_2H{\cdot}CCl(CO_2H){\cdot}CO_2H \longrightarrow CH_2Cl{\cdot}CO_2H$.

Methyl oximinocyanoacetate (Conrad and Schulze, A., 1909, i, 211) reacted with an equimolecular proportion of hydrazine hydrate in alcoholic solution, giving the *hydrazine* salt,

$$CN{\cdot}C(:NO{\cdot}N_2H_5){\cdot}CO_2Me,$$

a yellow, crystalline solid decomp. near 100° after sintering at 78°. When the reagents were heated together in alcoholic solution on a water-bath the product was the *hydrazine* salt, yellow needles, decomp. at 135°, of *oximinocyanoacetylhydrazine*, lustrous, brown leaflets, m. p. 166° (decomp.), the latter being liberated from the salt by careful treatment in the cold with the theoretical amount of hydrochloric acid; *silver* salt, brown; *lead* salt, brown; *hydrochloride*, yellow crystals, decomp. at 204°. If the hydrazine salt is treated in aqueous solution with benzaldehyde, benzaldazine, and *oximinocyanoacetylbenzylidenehydrazine*,

$$CN{\cdot}C(:NOH){\cdot}CO{\cdot}NH{\cdot}N:CHPh,$$

yellow needles, decomp. at 148°, are obtained, the latter compound being also produced by the action of benzaldehyde on oximinocyanoacetylhydrazine itself. The hydrazine salt reacts in an analogous manner with an excess of acetone, giving bisdimethylazimethylene and *oximinocyanoacetyl*iso*propylidenehydrazine*,

$$CN{\cdot}C(:NOH){\cdot}CO{\cdot}NH{\cdot}N:CMe_2,$$

compact, yellow, prismatic crystals, m. p. 205°. When the hydrazine salt of oximinocyanoacetylhydrazine is treated in concentrated aqueous solution under a layer of ether with sodium nitrite and dilute hydrochloric acid, *oximinocyanoacetylazide*,

$$CN{\cdot}C(:NOH){\cdot}CO{\cdot}N_3,$$

an explosive, yellow, crystalline solid of low m. p. is obtained, which reacts with sodium hydroxide solution and aniline respectively, giving sodium azoimide and oximinocyanoacetanilide (Dimroth and Dienstbach, A., 1909, i, 62), and with boiling alcohol yielding *oximinocyanomethylurethane*, $CN{\cdot}C(:NOH){\cdot}NH{\cdot}CO_2Et$, colourless, granular crystals, m. p. 96—97°. Hydrolysis of the last product with hydrochloric acid gives rise to carbon dioxide, alcohol, ammonia, hydroxylamine, and oxalic acid, the latter substances probably resulting from the decomposition of an intermediate amino-oximinoacetonitrile, $NH_2{\cdot}C(:NOH){\cdot}CN$.

Methyl nitrocyanoacetate, $CN{\cdot}CH(NO_2){\cdot}CO_2Me$, colourless, silky needles (with $1H_2O$), m. p. 76°, was obtained as its *potassium* salt, $CN{\cdot}C(:NO_2K){\cdot}CO_2Me$, lustrous leaflets, m. p. 264—266° (decomp.), by oxidation of methyl oximinocyanoacetate with potassium permanganate in aqueous solution; the free ester was liberated by converting it into the *silver* salt and decomposing with hydrogen sulphide. When treated in warm methyl-alcoholic solution with an equimolecular proportion of hydrazine hydrate, this ester gave a

yellow, crystalline, *hydrazine* salt, m. p. 168°, but with longer heating and a sesquimolecular quantity of hydrazine hydrate the product was the *hydrazine* salt, $CN\cdot C(NO_2\cdot N_2H_5)\cdot CO\cdot NH\cdot NH_2$, silky needles, m. p. near 200° (decomp.) after sintering near 140°, of nitrocyanoacetylhydrazine; this hydrazine salt when treated with benzaldehyde yielded benzaldazine and the free nitrocyanoacetylhydrazine. By treating the potassium salt of methyl nitrocyanoacetate with hydrazine hydrate, the analogous *potassium* salt, $CN\cdot C(NO_2K)\cdot CO\cdot NH\cdot NH_2$, long prisms, was obtained. *Nitrocyanoacetylhydrazide*, $CN\cdot CH(NO_2)\cdot CO\cdot NH\cdot NH_2$, obtained by the action of dilute hydrochloric acid on the above hydrazine or potassium derivative, forms colourless needles (with $1H_2O$) and can be recrystallised rapidly from warm water without alteration, but on boiling with water it is converted into the yellow, anhydrous compound, a similar dehydration being also effected in the hydrated salt by heating at 110—120°. The nitro-group renders nitrocyanoacetylhydrazide decidedly acidic in character, and it is probably to this cause that the noteworthy stability towards acids and alkalis is due; even when boiled with sodium hydroxide solution or dilute sulphuric acid for hours, no scission of hydrazine occurs, and even heating for six hours at 120—130° with hydrochloric acid in a sealed tube only causes a partial hydrolysis. When treated with excess of hydrazine hydrate the hydrated form of nitrocyanoacetylhydrazide gives the above-described colourless hydrazine salt, but the anhydrous compound yields a yellowish-red *isomeride*, decomp. at 200° after sintering at 185—195°, which, when its red, aqueous solution is acidified, regenerates the anhydrous form of the free compound, whereas under similar conditions the colourless hydrazine salt yields the hydrated compound. The *ammonium* salt also was obtained in an almost colourless form and in an orange-yellow form, both crystallising in needles. Indications were also obtained of the existence of a coloured modification of the potassium salt. This existence of two isomeric series of salts is regarded as analogous to the case of the nitroketones and dinitroparaffins (Hantzsch, A., 1907, i, 500, 555; Hantzsch and Voigt, A., 1912, i, 151; ii, 508).

By shaking with benzaldehyde in aqueous solution containing a little hydrochloric acid, nitrocyanoacetylhydrazine can be converted into the *benzylidene* derivative, $CN\cdot CH(NO_2)\cdot CO\cdot NH\cdot N\colon CHPh$, a microcrystalline powder which carbonises without melting, and is very readily resolved by warm water into benzaldehyde and nitrocyanoacetylhydrazide. Sodium nitrite in aqueous solution reacts with nitrocyanoacetylhydrazide, giving the *sodium* salt (yellow needles) of the *nitrocyanoacetylazide*, $CN\cdot CH(NO_2)\cdot CO\cdot N_3$, an almost colourless, crystalline, hygroscopic mass (with $1H_2O$) of low m. p., which was obtained by cautious treatment of the salt with dilute sulphuric acid. The azide gave an *aniline* salt,

$$C_9H_8O_3N_6,H_2O,$$

pale yellow, granular crystals, and when boiled with alcohol produced a brown, tarry mass which probably contained some of the expected urethane, as treatment with boiling hydrochloric acid gave rise to the formation of carbon dioxide, ammonia, and hydrogen

cyanide; in boiling aqueous solution also, nitrocyanoacetylazide decomposes vigorously, the products being similar to the final products from the treatment with hydrochloric acid, with the addition of carbon monoxide.

The above results indicate that with the introduction of the cyanoacetyl-, oximinocyanoacetyl-, and nitrocyanoacetyl-radicles into hydrazine this compound undergoes a gradual and regular weakening in basic character. D. F. T.

Preparations of Esters of Hydrazinemonocarboxylic Acid. E. MERCK (D.R.-P. 285800; from *J. Soc. Chem. Ind.*, 1915, **34**, 1167).—Reaction is brought about between equimolecular proportions of hydrazine hydrate and an ester of carbonic acid.

J. C. W.

Relations between the Constitution and the Physical Properties of Isomeric and of Homologous Hydroaromatic Compounds. K. VON AUWERS (*Annalen*, 1915, **410**, 287—336. Compare following abstract).—The author has collected from all trustworthy sources the magnitudes of the b. p.'s, densities, refractive indices, and exaltations of the specific refractions and dispersions of *cyclo*hexane, *cyclo*hexene, *cyclo*hexanol, and *cyclo*hexanone, and as far as possible of their mono-, di-, tri-, tetra-, and pentamethyl derivatives; in a few cases values for the methylene derivatives of *cyclo*hexene and its methyl homologues are recorded. The data have been sifted and tables compiled containing values, some of which are quite trustworthy, others are the most probable, and yet others are somewhat uncertain. Relations are then traced between these values and the constitutions of the various compounds. The most important of these are the following: In the case of isomeric compounds, (1) the b. p. of saturated alcohols and ketones falls when the methyl group is in proximity to the hydroxyl or carbonyl group; the b. p. of unsaturated hydrocarbons rises with approximation of the methyl group to the double linking. (2) The density in all four classes of compound increases with the packing of the methyl groups in the molecule and with their proximity to the double linking, the hydroxyl group, or the carbonyl group. (3) Similar relations hold, although less pronouncedly, for the refractive indices. (4) The molecular refraction of isomeric substances of all four classes is greater the farther are the side-chains from one another and from the double linking or the oxygenated group. (5) The molecular dispersion is normal in all saturated and in endocyclic, unsaturated compounds.

The preceding relations only hold for mono- and di-methyl derivatives; in the case of more highly methylated compounds generalisations cannot be made owing to lack of trustworthy data.

With regard to homologous compounds: (1) In *cyclo*hexanes and *cyclo*hexenes the introduction of methyl regularly causes an increase in the b. p., but in *cyclo*hexanols and *cyclo*hexanones such is frequently not the case. (2) As a rule the density of the oxygenated derivatives decreases as the number of methyl groups increases.

(3) No regularities can be traced for the refractive indices of homologous compounds, since here the constitutive influences are altogether predominant. It is noteworthy, however, that with few exceptions the value of n_D^{20} for all homologues of *cyclo*hexene is the same, about 1·445. C. S.

Simple Hydroaromatic Hydrocarbons, Alcohols, and Ketones. K. VON AUWERS, R. HINTERSEBER, and WILHELM TREPPMANN (*Annalen*, 1915, **410**, 257—287).—The compounds described in the paper are for the most part not new, but have been prepared in a state of great purity, and the magnitudes of various physical properties have been measured in order to correlate these with the constitutions; the saturated hydrocarbons and ketones are believed to be quite pure, but the authors do not guarantee that the alcohols and unsaturated hydrocarbons are free from possible stereoisomerides. The alcohols are hygroscopic, and the observation has been made that the density continuously increases when these are submitted to prolonged drying at a gentle heat in a current of hydrogen.

Phosphoric oxide is recommended for converting secondary carbinols into unsaturated hydrocarbons, and potassium hydrogen sulphate for tertiary carbinols. Saturated hydrocarbons are best obtained from secondary carbinols through the bromides.

*cyclo*Hexane has b. p. 80·0—80·2°/749 mm., $D_4^{11\cdot 2}$ 0·7869, n_α 1·42910, n_D 1·43119, n_β 1·43668, and n_γ 1·44116 at 10·85°. *cyclo*Hexene has b. p. 83—83·5°/760 mm., $D_4^{15\cdot 6}$ 0·8143, n_α 1·44653, n_D 1·44921, n_β 1·45620, and n_γ 1·46194 at 15·1°. Methylene*cyclo*hexane has b. p. 100·5—101·3°/756 mm., $D_4^{15\cdot 6}$ 0·8055, n_α 1·44934, n_D 1·45222, n_β 1·45958, and n_γ 1·46568 at 15·5°.

1 : 3-Dimethyl*cyclo*hexane, prepared by Crossley and Renouf's method (T., 1905, **87**, 1497), has b. p. 118—120°, $D_4^{21\cdot 8}$ 0·7701, n_α 1·42157, n_D 1·42398, n_β 1·42940, and n_γ 1·43394 at 22·0°.

1 : 2-Dimethyl-Δ^1-*cyclo*hexene has $D_4^{13\cdot 7}$ 0·8315, n_α 1·45906, n_D 1·46178, n_β 1·46908, and n_γ 1·47517 at 13·5°. 1 : 3-Dimethyl-Δ^3-*cyclo*hexene has b. p. 124—126°/760 mm., $D_4^{22\cdot 6}$ 0·7998, n_α 1·44263, n_D 1·44533, n 1·45215, and n_γ 1·45795 at 22·4°. 1 : 3-Dimethyl-Δ^5-*cyclo*hexene has b. p. 126—127°/746 mm., $D_4^{21\cdot 1}$ 0·797, n_α 1·44086, n_D 1·44361, n_β 1·45020, and n_γ 1·45587 at 21·1°. 1 : 4-Dimethyl-Δ^1-*cyclo*hexene has b. p. 124—126°/751 mm., $D_4^{22\cdot 4}$ 0·7985, n_α 1·44112, n_D 1·44372, n_β 1·45056, and n_γ 1·45626 at 22·0°.

Ethylidene*cyclo*hexane has b. p. 136·0—136·4°/766 mm., $D_4^{17\cdot 3}$ 0·8239, n_α 1·46094, n_D 1·46389, n_β 1·47139, and n_γ 1·47773 at 17·6°.

1 : 3 : 5-Trimethyl*cyclo*hexene, b. p. 139—141°/766 mm., $D_4^{24\cdot 7}$ 0·7941, n_α 1·44102, n_D 1·44378, n_β 1·45057, and n_γ 1·45638 at 24·7°, reacts with hydrogen chloride and with hydrogen bromide in cooled glacial acetic acid to form 1 : 3 : 5-*trimethyl*cyclo*hexyl chloride*, b. p. 68—69°/20 mm., $D_4^{15\cdot 5}$ 0·9217, n_α 1·45182, n_D 1·45455, n_β 1·46035, and n_γ 1·46555 at 15·2°, and the *bromide*, b. p. 95—98°/23 mm., $D_4^{11\cdot 1}$ 1·1749, n_α 1·47951, n_D 1·48280, n_β 1·48971, and n_γ 1·49532 at 11·1°; neither of these derivatives could be satisfactorily converted into 1 : 3 : 5-trimethyl*cyclo*hexane.

1 : 3-*Dimethyl-5-methylene*cylo*hexane*, $C_6H_8Me_2\colon CH_2$, prepared by heating 1 : 3-dimethyl*cyclo*hexylidene-5-acetic acid at about 220° in a slow current of carbon dioxide, has b. p. 135—136°/744 mm., $D_4^{14\cdot6}$ 0·7918, n_α 1·44334, n_D 1·44628, n_β 1·45313°, and n_γ 1·45917 at 14·6°, and yields 1 : 3-dimethyl*cyclo*hexan-5-one by oxidation with faintly alkaline 2% potassium permanganate.

*cyclo*Hexanol has m. p. 23°, $D_4^{37\cdot0}$ 0·9373, n_α 1·45902, n_D 1·46055, n_β 1·46685, and n_γ 1·47146 at 37·0°. 1-Methyl*cyclo*hexanol has m. p. 24—25°, b. p. 56·5°/10 mm., $D_4^{24\cdot65}$ 0·9251, n_α 1·45631, n_D 1·45874, n_β 1·46428, and n_γ 1·46908 at 24·65°.

1-Methyl*cyclo*hexan-2-ol has b. p. 167·4—167·6°, $D_4^{13\cdot4}$ 0·9333, n_α 1·46352, n_D 1·46585, n_β 1·47180, and n_γ 1·47665 at 13·4°. 1-Methyl*cyclo*hexan-3-ol has b. p. 76—78°/14 mm., $D_4^{24\cdot3}$ 0·9182, n_α 1·45217, n_D 1·45444, n_β 1·46031, and n_γ 1·46502 at 24·3°. 1-Methyl*cyclo*hexan-4-ol has b. p. 74·7—75·2°/12 mm., $D_4^{22\cdot5}$ 0·9183, n_α 1·45366, n_D 1·45594, n_β 1·46160 and n_γ 1·46651 at 22·5°.

1 : 3-Dimethyl*cyclo*hexan-3-ol has b. p. 79—81°/21 mm., $D_4^{22\cdot9}$ 0·9028, n_α 1·45177, n_D 1·45414, n_β 1·45984, and n_γ 1·46463 at 22·9°. 1 : 4-Dimethyl*cyclo*hexan-4-ol has b. p. 70—72°/19 mm. (Sabatier and Mailhe and also Wallach have obtained this substance in the solid state), $D_4^{23\cdot9}$ 0·9060, n_α 1·45317, n_D 1·45534, n_β 1·46141, and n_γ 1·46622 at 23·9°. 1 : 3-Dimethyl*cyclo*hexan-5-ol has m. p. 36—38° (other preparations remained liquid), $D_4^{38\cdot4}$ 0·8810, n_α 1·44440, n_D 1·44700, n_β 1·45238, and n_γ 1·45727 at 38·4°. 1 : 3 : 5-Trimethyl*cyclo*hexan-5-ol has b. p. 82—83°/19 mm., $D_4^{16\cdot3}$ 0·8880, n_α 1·45108, n_D 1·45371, n_β 1·45921, and n_γ 1·46422 at 16·3°.

*cyclo*Pentanone has b. p. 23·2—23·6°/10 mm., $D_4^{17\cdot3}$ 0·9513, n_α 1·43587, n_D 1·43817, n_β 1·44390, and n_γ 1·44867 at 17·3°. *cyclo*Hexanone has b. p. 156·6—156·8°, $D_4^{15\cdot3}$ 0·9503, n_α 1·45024, n_D 1·45261, n_β 1·45859, and n_γ 1·46370 at 15·3°. *cyclo*Heptanone has $D_4^{21\cdot9}$ 0·9495, n_α 1·45801, n_D 1·46027, n_β 1·46646, and n_γ 1·47149 at 21·9°.

1-Methyl*cyclo*hexan-2-one has b. p. 167°/740 mm., $D_4^{14\cdot6}$ 0·9300, n_α 1·44827, n_D 1·45049, n_β 1·45653, and n_γ 1·46135 at 14·6°. 1-Methyl*cyclo*hexan-3-one has b. p. 60—60·2°/15 mm., $D_4^{25\cdot15}$ 0·9139, n_α 1·44092, n_D 1·44313, n_β 1·44914, and n_γ 1·45394 at 25·15°. 1-Methyl*cyclo*hexan-4-one has b. p. 55·8—56·4°/10·5 mm., $D_4^{24\cdot4}$ 0·9119, n_α 1·44092, n_D 1·44322, n_β 1·44918, and n_γ 1·45413 at 24·4°. 1 : 3-Dimethyl*cyclo*hexan-5-one has b. p. 180°, $D_4^{14\cdot7}$ 0·8962, n_α 1·44270, n_D 1·44492, n_β 1·45101 and n_γ 1·45579 at 14·7°. C. S.

Thermal Reactions of Aromatic Hydrocarbons in the Vapour Phase. W. F. Rittman, O. Byron, and G. Egloff (*J. Ind. Eng. Chem.*, 1915, **7**, 1019—1024. Compare this vol., i, 1).—The decomposition of aromatic hydrocarbons when heated in the vapour phase proceeds in the direction cymene ⟶ xylene ⟶ toluene ⟶ benzene ⟶ naphthalene ⟶ anthracene ⟶ tarry matter, carbon, and gas, and scarcely appreciably in the reverse direction. Any one hydrocarbon, therefore, gives rise to any or all of the products following it in the above scheme, according to conditions, and not to any of those preceding it. The paper is fully illustrated with

tables showing the quantitative results of the cracking experiments. G. F. M.

Some Aromatic Fluoro-derivatives and the Nitration of *p*-Fluorochlorobenzene. FRED. SWARTS (*Rec. trav. chim.*, 1915, **35**, 131—153).—A quantitative study of the nitration of *p*-fluorochlorobenzene, a number of fluoro-compounds being prepared and used for the identification of the products of nitration. The *p*-fluorochlorobenzene used was prepared from *p*-fluoroaniline by Gatterman's reaction. It had m. p. −26·9°; b. p. 130·15°/757·3 mm. (corr.); D^0 1·2573; $D^{11\cdot2}$ 1·2355; $n_{\alpha}^{11\cdot2}$ 1·49432; $n_{\beta}^{11\cdot2}$ 1·50957; $n_{\gamma}^{11\cdot2}$ 1·52085; $n_{D}^{11\cdot2}$ 1·49890 (compare Wallach and Heusler, A., 1888, 362). 6-*Fluoro*-3-*chloro*-1-*nitrobenzene* is prepared by diazotising 4-fluoro-3-nitroaniline in solution in concentrated hydrochloric acid. It crystallises from light petroleum in colourless prisms, m. p. 10·2°, b. p. 138·5/29 mm., and is readily decomposed by aqueous alkali hydroxides, giving the corresponding salts of 4-chloro-2-nitrophenol. With sodium methoxide at 25°, the fluorine atom is replaced by the group ·OMe, and with alcoholic ammonia 4-chloro-2-nitroaniline is obtained.

Attempts to prepare 5-*fluoro*-2-*chloro*-1-*nitrobenzene* by the action of phosphorus pentachloride on 4-fluoro-2-nitrophenol were not successful, but it was finally obtained from the corresponding fluoronitroaniline. *p*-Fluoroacetanilide when nitrated with acetyl nitrate in acetic acid solution at 0° yielded 4-*fluoro*-2-*nitroacetanilide*, pale yellow prisms, m. p. 71·5°, which on hydrolysis with dilute hydrochloric acid gave 4-*fluoro*-2-*nitroaniline*, orange-coloured, prismatic crystals, m. p. 92·45°. This aniline when submitted to Gatterman's reaction gave 5-*fluoro*-2-*chloro*-1-*nitrobenzene*, prisms, m. p. 37·25°; b. p. 238·5°. It is much more resistant to the action of alkalis than its isomeride, being unacted on in the cold, but when heated with sodium methoxide in a sealed tube at 110° for thirty hours both the chlorine and the fluorine atoms were removed and the substance resinified.

p-Fluorochlorobenzene was nitrated by slowly adding it to concentrated nitric acid cooled to −10°, the temperature not being allowed to rise above −7°, the product being finally poured on to ice. The unchanged fluorochlorobenzene was distilled off under reduced pressure and a small amount of 2-chloro-5-nitrophenol formed was removed by washing with a solution of sodium carbonate. The final nitrated mixture had a solidification point 23·75°, and was analysed first by decomposition of the 6-fluoro-3-chloro-1-nitrobenzene with sodium methoxide at 25°, and secondly by preparing the solidification-point curve of mixtures of the pure isomerides. The two methods agree in showing that in the nitration the NO_2 group enters the ortho-position to the chlorine to the extent of 62·25% and into the ortho-position to the fluorine to the extent of 27·75%.
W. G.

***m*-Difluorobenzene and its Nitration.** FRED. SWARTS (*Rec. trav. chim.*, 1915, **35**, 154—165).—*m*-Difluorobenzene is readily

obtained by the diazotisation of *m*-fluoroaniline in hydrofluoric acid solution, followed by distillation. It has b. p. 82·8—82·85°/757·3 mm., 82·2°/742 mm. (corr.); $D^{15\cdot5}$ 1·1651; $n_{\alpha}^{15\cdot5}$ 1·43601; $n_{\beta}^{15\cdot5}$ 1·44871; $n_{\gamma}^{15\cdot5}$ 1·45628. It was nitrated by slowly adding it to concentrated nitric acid at −4—0°, the product being poured on to ice after one hour. When purified the product had m. p. 9·52°; $D^{13\cdot9}$ 1·4577; $n_{\alpha}^{12\cdot4}$ 1·50998; $n_{\beta}^{12\cdot4}$ 1·53220, and was mainly 2:4-difluoro-1-nitrobenzene with a trace of some other compound. A determination of the depression of the freezing point of pure 2:4-difluoro-1-nitrobenzene by the addition of fluorodinitrobenzene, showed that the original nitration product contained at the most 0·434% of 1:3-difluoro-2-nitrobenzene. 2:4-Difluoro-1-nitrobenzene is decomposed by sodium methoxide, giving 5-*fluoro*-2-*nitroanisole*, m. p. 48·8°, b. p. 272°, together with some 4-nitroresorcinol, m. p. 73°. When reduced with iron in the presence of sulphuric acid the difluoronitrobenzene yielded 2:4-*difluoroaniline*, m. p. −7·5°, b. p. 169·5°/753 mm., giving 2:4-*difluoroacetanilide*, m. p. 120·9°.

When nitrated in the warm or at 100° by nitric acid (D 1·52) and sulphuric acid, *m*-difluorobenzene yielded quantitatively 4:6-*difluoro*-1:3-*dinitrobenzene*, colourless prisms, m. p. 74°. With sodium methoxide at the ordinary temperature it yielded the dimethyl ether of 4:6-dinitroresorcinol, m. p. 155·4°, and with alcoholic ammonia in excess at the ordinary temperature 4:6-dinitro-*m*-phenylenediamine, m. p. 296°. Using only 2 mols. of ammonia the product was 3-*fluoro*-4:6-*dinitroaniline*, m. p. 186·6°, together with a small amount of 4:6-*dinitro*-m-*phenetidine*, m. p. 169°. W. G.

Preparation of [Chlorine] Substituted Products of Toluene. L. Cassella & Co. (Eng. Pat. 16317 (1914); from *J. Soc. Chem. Ind.*, 1915, **34**, 1203).—Dry chlorine is passed over dry toluene in presence of anhydrous iron chloride at 12—15°, the mixture being stirred. When the trichlorotoluene which is thus formed crystallises out, the temperature is raised to 35°, gradually increasing to 50°, and treatment with chlorine is continued until the necessary increase in weight has occurred. On fractional distillation, a yield of 90% of the theory of tetrachlorotoluene is obtained. Only traces of the pentachloro-compound are produced, as indicated by the slight precipitation on diluting a sample with an equal volume of carbon disulphide. Further chlorination of tetrachlorotoluene at 100—130° in violet or ultraviolet light gives tetrachlorobenzylidene chloride. G. F. M.

Reactions in Energetic Solvents. I. The Direct Replacement of Sulpho-groups by Chlorine. Hans Meyer (*Monatsh.*, 1915, **36**, 719—722).—In 1860 Carius observed that methane- and ethane-sulphonyl chlorides when heated at 150—160° with phosphorus pentachloride underwent change according to the equation $R\cdot SO_2Cl + PCl_5 = RCl + SOCl_2 + POCl_3$. The author has now discovered that thionyl chloride is especially favourable to the scission of sulphur dioxide from sulphonyl chlorides, and he believes that thionyl chloride was largely instrumental in producing the results obtained by Carius.

At 160—180° in the presence of thionyl chloride, aromatic sulphonic acids, as also their chlorides and anhydrides, are converted into the corresponding chloro-compounds with liberation of sulphur dioxide. Thus *p*-chlorobenzenesulphonic acid quantitatively yielded *p*-dichlorobenzene and sodium benzenesulphonate gave chlorobenzene. With derivatives of the anthraquinone group the necessary temperature is higher and at 200—220° the α- and β-sulphonic acids derived from anthraquinone were converted into the corresponding chloroanthraquinones.

In the absence of thionyl chloride, whether other solvents, such as tetrachloroethane, are present or not, the decomposition of the sulphonyl chlorides is only partial and frequently more complex in nature. D. F. T.

Reactions in Energetic Solvents. II. The Direct Replacement of Nitro-groups by Chlorine and a New Method of Chlorination. HANS MEYER (*Monatsh.*, 1915, **36**, 723—730. Compare preceding abstract).—Other substituents in aromatic compounds besides the sulphonyl group can be replaced by chlorine under the influence of thionyl chloride, the present publication only giving results on the replacement of the nitro-group. 4-Chloro-3-nitrobenzenesulphonic acid, *p*-chloronitrobenzene, 2:5-dichloronitrobenzene, and nitrobenzene when heated with thionyl chloride at temperatures between 140° and 180° lost their nitro-groups almost quantitatively with formation of 1:2:4-trichlorobenzene, *p*-dichlorobenzene, 1:2:4-trichlorobenzene, and chlorobenzene respectively. With *m*-nitrobenzenesulphonic acid the yield of *m*-dichlorobenzene was not so good, direct chlorination occurring simultaneously to some extent, so that the product also included a substance, m. p. 165—175°, containing a high percentage of chlorine. A similar result was obtained with *o*-nitroanisole, which gave a trichlorophenol in addition to *o*-chloroanisole.

1:5-Dinitroanthraquinone at 180—200° was converted into 1:5-dichloroanthraquinone, but with naphthalene compounds chlorination occurred very readily, naphthalene itself at 170—180° reacting with thionyl chloride giving 1:4-dichloronaphthalene. The presence of certain groups facilitates direct chlorination even of the benzene nucleus; azobenzene reacts with thionyl chloride at 180—200°, giving 2:2′-dichloroazobenzene, together with its 4:4′-isomeride.

At somewhat higher temperatures, namely, 230—250°, the successive substitution of the hydrogen atoms of a methyl radicle attached to an aromatic nucleus may be effected; thus toluene gave benzylidene dichloride and benzotrichloride, whilst α-methylanthraquinone yielded the monochloro- and dichloro-methyl derivatives. By the use of suitable solvents, however, the methyl group in such substances as toluenesulphonic acids may be protected so that the action of the thionyl chloride is restricted to the replacement of the sulphonic group by chlorine. D. F. T.

Sulphonation of Benzene. II. GERHARD MOHRMANN (*Annalen*, 1915, **410**, 373—385).—The catalytic influence of sodium, mercury,

and iron on the sulphonation of benzene has been described by Behrend and Mertelsmann (A., 1911, i, 189). The author has examined the influence of members of the other groups of the periodic table, namely, aluminium, lead, arsenic, selenium, and manganese, and also of cadmium and bismuth. Benzene vapour is passed into 97% sulphuric acid at 235—245° containing the catalyst, and the resulting *m*- and *p*-benzenedisulphonic acids (and in the case of lead the monosulphonic acid also) are converted through the sodium salts into the acid chlorides, the crystals of which are separated mechanically.

The results show that none of the substances approaches mercury in its catalytic effect. Manganese has scarcely any influence and cadmium has but little more. The other catalysts produce about the same effects with the exceptions of selenium, which in the form of selenious acid causes carbonisation (although at 160—170° it has no effect, benzenesulphonic acid only being produced), and of lead, which in the form of lead sulphate brings about the formation of 80·8% of the meta-disulphonic acid, 9·7% of the para-acid, and 9·5% of the monosulphonic acid. C. S.

***N*-Halogen Derivatives of the *p*-Halogen-substituted Benzenesulphonamides.** ROBERT REGINALD BAXTER and FREDERICK DANIEL CHATTAWAY (T., 1915, **107**, 1814—1823).—The soluble sodium salts of various sulphonmonochloroamides have recently received considerable attention owing to their use in the treatment of infected wounds. Simple compounds of this nature were described some years ago (T., 1905, **87**, 145) and a number of *p*-halogen-substituted substances have now been prepared. The sulphondihalogenoamides are obtained by the action of the acids, HOX, on the amides, and these give the sodium salts of the sulphonmonohalogenoamides when treated with sodium hydroxide.

The sodium salts of the *p*-halogenobenzenesulphonic acids which were required for the preparation of the sulphonyl chlorides were obtained by gradually adding the halogenobenzene to fuming sulphuric acid (10% SO_3) at below 60°, and then pouring the cold solution into brine at 0°. The salts were dried and separated from sodium chloride by solution in alcohol, and then converted into the chlorides by grinding with phosphorus pentachloride.

p-*Chlorobenzenesulphondichloroamide*, $C_6H_4Cl\cdot SO_2\cdot NCl_2$, crystallises in colourless, rhombic prisms, m. p. 83°, and the dibromoamide in pale yellow, six-sided, rhombic prisms, m. p. 102° (compare Kastle, Keiser, and Bradley, A., 1896, i, 555). *Potassium* p-*chlorobenzenesulphonchloroamide*, $C_6H_4Cl\cdot SO_2K{:}NCl,H_2O$, forms glistening, elongated prisms, which lose water and then decompose violently at about 160°; the *sodium* salt also crystallises with $1H_2O$ and decomposes violently at about 190°.

p-Bromobenzenesulphondichloroamide (*ibid.*) gives *potassium* p-*bromobenzenesulphonchloroamide*, colourless needles, with $1H_2O$, which explode at 165°, and the *sodium* salt, $1H_2O$, explosion p. 178°. p-*Bromobenzenesulphondibromoamide* crystallises in pale yellow, elongated, rhombic prisms, m. p. 132—133° (decomp.), and yields

the salts of *p*-bromobenzenesulphonbromoamide; *potassium*, $1H_2O$, explosion p. 193°; *sodium*, $1H_2O$, expl. p. 211°.

p-*Iodobenzenesulphondichloroamide* crystallises in elongated, rhombic prisms, m. p. 147°, and gives the salts of *p*-iodobenzene sulphonchloroamide; *potassium*, $1H_2O$, expl. p. 150°; *sodium*, $1H_2O$, expl. p. 185°.

p-*Chlorobenzenesulphonmethylamide*, $C_6H_4Cl\cdot SO_2\cdot NHMe$, forms shining, white plates, m. p. 59°, and yields the *chloroamide*, $C_6H_4Cl\cdot SO_2\cdot NMeCl$, six-sided, rhombic prisms, m. p. 66°, and the *bromoamide*, pale yellow, rhombic prisms, m. p. 99°. p-*Chlorobenzenesulphonbenzylamide*, $C_6H_4Cl\cdot SO_2\cdot NH\cdot CH_2Ph$, crystallises in white needles, m. p. 108—109°, and forms the *chloroamide*, rhombic prisms, m. p. 124°, and *bromoamide*, m. p. 112°.

The sulphonyl chlorides were also condensed with various anilines, and a large number of sulphonanilides and their corresponding chloroamides are described.

p-*Chlorobenzenesulphonphenylchloroamide*, $C_6H_4Cl\cdot SO_2\cdot NPhCl$, forms six-sided rhombic prisms, m. p. 100°; p-*bromobenzenesulphonphenylchloroamide* crystallises in elongated rhombic prisms, m. p. 104°, and the p-*iodo*-compound in colourless rhombs, m. p. 139—140°.

The p-*chlorobenzenesulphonyl* derivatives of substituted anilines are as follows: -m-*chloroanilide*, transparent rhombs, m. p. 106°; -m-*chlorophenylchloroamide*, $C_6H_4Cl\cdot SO_2\cdot NCl\cdot C_6H_4Cl$, rhombic prisms, m. p. 90°; -p-*chloroanilide*, needles, m. p. 148°; -p-*chlorophenylchloroamide*, prisms, m. p. 127°; -2:4-*dichloroanilide*, plates, m. p. 108°; -2:4-*dichlorophenylchloroamide*, prisms, m. p. 100°; p-*bromoanilide*, prisms, m. p. 163°; -p-*bromophenylchloroamide*, prisms, m. p. 127°; -2:4-*dibromoanilide*, prisms, m. p. 116°; -2:4-*dibromophenylchloroamide*, prisms, m. p. 110° (decomp.); -p-*iodoanilide*, prisms, m. p. 173°; -p-*iodophenylchloroamide*, very unstable, m. p. 70° (decomp.); -o-*nitroanilide*, pale yellow prisms, m. p. 114° (decomp.); -o-*nitrophenylchloroamide*, prisms, m. p. 148° (decomp.); -m-*nitroanilide*, pale yellow needles, m. p. 124°; -m-*nitrophenylchloroamide*, almost colourless prisms, m. p. 131° (decomp.); -p-*nitroanilide*, yellow needles, m. p. 159° (decomp.); -p-*nitrophenylchloroamide*, prisms, m. p. 143° (decomp.); -o-*toluidide*, colourless needles, m. p. 111°; -o-*tolylchloroamide*, prisms, m. p. 127° (decomp.); -p-*toluidide*, prisms, m. p. 88°; -p-*tolylchloroamide*, prisms, m. p. 110° (decomp.); -p-*tolylbromoamide*, pale yellow prisms, m. p. 91°.

The p-*bromobenzenesulphonyl* derivatives are as follows: -p-*chloroanilide*, $C_6H_4Br\cdot SO_2\cdot NH\cdot C_6H_4Cl$, prisms, m. p. 138°; -p-*chlorophenylchloroamide*, prisms, m. p. 142°; -2:4-*dichloroanilide*, prisms, m. p. 134°; -2:4-*dichlorophenylchloroamide*, prisms, m. p. 97°; -p-*bromoanilide*, prisms, m. p. 141°; -p-*bromophenylchloroamide*, prisms, m. p. 141°; -2:4-*dibromoanilide*, prisms, m. p. 147°; -2:4-*dibromophenylchloroamide*, prisms, m. p. 117°; -p-*iodoanilide*, prisms, m. p. 160° (decomp.); -p-*iodophenylchloroamide*, very unstable, decomp. below 100°; -o-*nitroanilide*, yellow needles, m. p. 130°; -o-*nitrophenylchloroamide*, prisms, m. p. 160° (decomp.);

-m-*nitroanilide*, yellow needles, m. p. 140°; -m-*nitrophenylchloroamide*, long, yellow prisms, m. p. 140° (decomp.); -p-*nitroanilide*, needles, m. p. 183°; -p-*nitrophenylchloroamide*, prisms, m. p. 164°; -o-*toluidide*, prisms, m. p. 119°; -o-*tolylchloroamide*, prisms, m. p. 129° (decomp.); -p-*toluidide*, prisms, m. p. 99°; -p-*tolylchloroamide*, prisms, m. p. 131°.

The *p-iodobenzenesulphonyl* derivatives are as follows: -p-*bromoanilide*, rhombic plates, m. p. 174°; -p-*bromophenylchloroamide*, $C_6H_4I\cdot SO_2\cdot NCl\cdot C_6H_4Br$, prisms, m. p. 137° (decomp.); -p-*iodoanilide*, glistening plates, m. p. 167° (decomp.); -p-*iodophenylchloroamide*, very unstable, m. p. 142° (decomp.); -o-*nitroanilide*, very pale yellow plates, m. p. 137°; -o-*nitrophenylchloroamide*, very pale yellow prisms, m. p. 167°; -m-*nitroanilide*, long, yellow prisms, m. p. 157°; -m-*nitrophenylchloroamide*, prisms, m. p. 164°; -p-*nitroanilide*, glistening plates, m. p. 154°; -o-*toluidide*, long plates, m. p. 161°; -o-*tolylchloroamide*, prisms, m. p. 110°; -p-*toluidide*, prisms, m. p. 135°; -p-*tolylchloroamide*, prisms, m. p. 137° (decomp.).

J. C. W.

Nitrophenanthrenes. ADOLFO MELÓN (*Anal. Fis. Quim.*, 1915, **13**, 381—389).—A preliminary note describing the influence of the experimental conditions on the nitration of phenanthrene.

A. J. W.

A New Transformation of Acenaphthylene, and Synthesis of Diacenaphthylidene, a New Yellow Hydrocarbon. J. DOLIŃSKI and K. DZIEWOŃSKI (*Ber.*, 1915, **48**, 1917—1931).—The polymerisation of acenaphthylene under the influence of light and heat demonstrated the extreme lability of the substance (compare A., 1912, i, 844; 1913, i, 847; 1914, i, 825). This is still further exemplified when the hydrocarbon is treated with traces of mineral acids, for two other polymerides result. One of them is believed to be diacenaphthylidene, $C_{10}H_6<\begin{matrix}C{=\!=}C{-}{-}{-}\\ | \quad\;\; | \\ CH_2\;CH_2\end{matrix}>C_{10}H_6$, whilst the other is a complex substance, at least a pentameride.

A solution of acenaphthylene in glacial acetic acid (50 grams to 120 grams) was mixed with 0·5 c.c. of concentrated hydrochloric acid, and then warmed for an hour or two on the water-bath. The clear liquid gradually deposited a pale yellow, heavy precipitate (40 grams) which was separated into the component polymerides by means of benzene, the complex one being freely soluble. A better yield of the dimeride was obtained by treating the picrate of acenaphthylene with hydrochloric acid.

7:7-*Diacenaphthylidene* (*dinaphthylenebutene*), $C_{24}H_{16}$, was obtained in golden-yellow, glistening leaflets or tablets, m. p. 277° (corr.), which gave a greenish-blue solution in concentrated sulphuric acid. Very dilute solutions in the aromatic hydrocarbons (for example, a 0·00125% solution in benzene) exhibited a very intense violet-blue fluorescence, which disappeared in bright sunlight, owing to oxidation of the hydrocarbon. The *dipicrate* was obtained in

dark red needles, m. p. 216—217°. The constitution of the hydrocarbon was ascertained by oxidation with sodium dichromate and acetic acid to naphthalic anhydride, and by reduction with red phosphorus and hydriodic acid to 7:7-diacenaphthyl (*loc. cit.*).

Bromine was not absorbed directly by the hydrocarbon, but acted substitutively. On warming the substance with a solution of bromine in carbon disulphide, it was transformed into 8:8-*dibromodiacenaphthylidene*, $\begin{matrix} C_{10}H_6 \\ | \\ CHBr \end{matrix} \!\!>\! C\!:\!C \!<\!\! \begin{matrix} C_{10}H_6 \\ | \\ CHBr \end{matrix}$, ciliated, orange-yellow needles, decomp. 203°, which was oxidised to naphthalic anhydride. In the cold, however, substitution in the naphthalene residues took place, the product being *αα'-dibromodiacenaphthylidene*, $C_{24}H_{14}Br_2$, ciliated yellow needles, m. p. 310° (decomp.), which was oxidised to α-bromonaphthalic anhydride. A fine suspension of the hydrocarbon in acetic acid was also treated with nitric acid (D 1·5) when *αα'-dinitrodiacenaphthylidene*, $C_{24}H_{14}O_4N_2$, was obtained in dark red, glistening needles, which decomposed without melting at above 360°, and were oxidised to α-nitronaphthalic anhydride.

In the polymerisation of acenaphthylene itself, the chief product (70—80% yield) was the complex polymeride. This differs from the polyacenaphthylene obtained by thermo-polymerisation (*loc. cit.*) in m. p., and in being readily soluble in acetone and easily oxidised to naphthalic anhydride, and it is therefore designated allo-*polyacenaphthylene*. It was obtained as an amorphous, yellow substance, m. p. 185—190°, approximating to the formula $C_{60}H_{40}$.

J. C. W.

Some New Organic Compounds of Vanadium. A. T. MERTES and HERMAN FLECK (*J. Ind. Eng. Chem.*, 1915, **7**, 1037—1038).—When treated in the cold variously in carbon tetrachloride or benzene solution, vanadium tetrachloride formed insoluble additive compounds with certain organic bases. The following were isolated in an analytically pure condition: With aniline, a black powder of the composition $4NH_2Ph,VCl_4$; with dimethylaniline, a green tar having the formula $4NMe_2Ph,VCl_4$; with phenylhydrazine, a violet substance of constitution similar to the above; with toluidine, ammonia, methylamine, and diphenylamine, products were obtained approximating to the formulæ $3C_6H_4Me{\cdot}NH_2,VCl_4$, $4NH_3,VCl_4,4H_2O$, $6NH_2Me,VCl_4,H_2O$, and $3NHPh_2,2VCl_4$ respectively. A solution of vanadium tetrachloride in benzene deposited, on keeping, a purple compound with evolution of hydrogen chloride. It varied in composition according to the length of time the solution was kept. Anthracene also formed a similar substitution product. Vanadium was estimated in the above compounds in the filtrate obtained from a lime fusion after precipitation of the chlorine with silver nitrate, by precipitating as lead vanadate, dissolving this in nitric acid and evaporating with sulphuric acid to remove the lead, reducing with sulphur dioxide, and titrating the hot solution, freed from excess of sulphurous acid, with $N/20$-permanganate. G. F. M.

Monotropic Polymorphic Anilides. FREDERICK DANIEL CHATTAWAY and WILLIAM JAMES LAMBERT (T., 1915, **107**, 1766—1773).—A close study of the behaviour of anilides when crystallising suggests that all anilides are capable of forming three very distinct types of crystals, namely, very slender, hair-like crystals, slender needles or prisms, and stout, compact crystals. A large number of anilides can be made to crystallise in two of these forms, and some have been obtained in all three varieties. For example, when *p*-bromoacetanilide and 2:4-dibromoacetanilide are allowed to crystallise from hot alcoholic solutions, they separate in long needles, which slowly give place to the stable, compact form. The rate of transformation varies with the solvent and the anilide used and increases rapidly with the temperature. Between 0° and the m. p., the compact form is stable, and the solids, therefore, show no transition point within these limits. The view is held, however, that the transition point is much below the ordinary temperature, but is unrecognisable because of the slow rate of the change. The point could be determined by measuring the solubilities of the two forms over a considerable range of temperature, but this is a matter of extreme difficulty, owing to the rapidity of transformation in the warm solutions. Within the limits which have been found practicable, the solubility curves for the two modifications are parallel, and, therefore, the two anilides are provisionally classed as monotropic.

The development of the crystals is illustrated by photographs, and the paper also records careful determinations of the solubilities of *p*-chloro-, 2:4-dichloro-, *p*-bromo-, 2:4-dibromo-, 4-chloro-2-bromo-, and 2-chloro-4-bromo-acetanilides, in alcohol at from 5° to 45°. J. C. W.

Phenyl Esters of Oxalic Acid. ROGER ADAMS and H. GILMAN (*J. Amer. Chem. Soc.*, 1915, **37**, 2716—2720).—Aryl oxalates can be prepared in almost quantitative yield by adding oxalyl chloride (5 grams) to ice-cold pyridine (25 c.c.), crushing well the resulting additive compound, and gradually adding the phenol (2 mols.) dissolved in a few c.c. of pyridine. The mixture is kept at 0° for two hours and is then poured into a mixture of concentrated hydrochloric acid and ice, when the ester is precipitated. In addition to the normal oxalates derived from *p*-cresol, α- and β-naphthols, and guaiacol, the following esters were prepared: o-*Nitrophenyl oxalate*, $C_2O_4(C_6H_4{\cdot}NO_2)_2$, yellow needles, m. p. 185°; o-*aldehydophenyl oxalate*, $C_2O_4(C_6H_4{\cdot}CHO)_2$, plates, m. p. 153–154°; *vanillyl oxalate*, $C_2O_4[C_6H_3(OMe){\cdot}CHO]_2$, crystals, m. p. 203–204°; β-*acetyl*-α-*naphthyl oxalate*, $C_2O_4(C_{10}H_6Ac)_2$, leafy crystals, m. p. 197°; o-*carbomethoxyphenyl oxalate*, $C_2O_4(C_6H_4{\cdot}CO_2Me)_2$, needles, m. p. 158°. Quinol gave rise to an *oxalate*, $C_2O_4(C_6H_4{\cdot}OH)_2$, m. p. 212°, but if the reaction was allowed to occur without cooling, a mixture was obtained from which, after treatment with acetic acid, needles, m. p. 226°, could be isolated, probably of the acetate of di-*p*-hydroxyphenyl ether, $C_{14}H_{12}O_4$. D. F. T.

Preparation of 6-Nitro-3-aminophenol and its Methyl Ether. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 285638; from *J. Soc. Chem. Ind.*, 1915, **34**, 1135).—When 4-nitro-1-acetylaminobenzene-3-sulphonic acid (nitroacetylsulphanilic acid) is heated at a high temperature, under pressure, with methyl-alcoholic alkali, the acetyl group is saponified, and the sulphonic acid group is replaced by hydroxyl or methoxyl. J. C. W.

***m*-Phenetidine and Some of its Derivatives.** FRÉDÉRIC REVERDIN and J. LOKIETEK (*Bull. Soc. chim.*, 1915, [iv], **17**, 406—409. Compare A., 1915, i, 878).—*m*-Phenetidine has been prepared by a new method, and from it a number of derivatives have been obtained.

Acetyl-*m*-aminophenol, when heated for two hours in alcoholic solution with sodium hydroxide and ethyl bromide, is readily ethylated, giving *aceto*-m-*phenetidide*, $OEt\cdot C_6H_4\cdot NH\cdot COMe$, greyish-white plates, m. p. 96—97°. Ethyl sulphate can also be used for the ethylation. This acetyl derivative is readily hydrolysed by heating on a water-bath with 35% hydrochloric acid, giving the free base yielding a *hydrochloride*, colourless leaflets, and a *picrate*, yellow needles, m. p. 158°. The following acyl derivatives have been prepared by the usual methods: *Formyl-m-phenetidide*, $OEt\cdot C_6H_4\cdot NH\cdot COH$, m. p. 52°; *benzo*-m-*phenetidide*,

$$OEt\cdot C_6H_4\cdot NH\cdot COPh,$$

long, white needles, m. p. 103°; *toluene*-p-*sulpho*-m-*phenetidide*, $OEt\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_6H_4Me$, yellowish-white leaflets, m. p. 157°; o-*nitrotoluene*-p-*sulpho*-m-*phenetidide*,

$$OEt\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_6H_3Me\cdot NO_2,$$

needles, m. p. 88°, and 2′ : 4′-*dinitro*-3-*ethoxydiphenylamine*, $OEt\cdot C_6H_4\cdot NH\cdot C_6H_3(NO_2)_2$, orange-yellow crystals, m. p. 151°.

m-Phenetidine has been diazotised and coupled with β-naphthol, giving a *compound*, $C_{18}H_{15}O_2N_2$, red needles, m. p. 107°, yielding a *sodium* salt insoluble in cold water. Coupled with salicylic acid, the diazo-salt gives a *compound* which dyes wool bright yellow; coupled with resorcinol, a *compound*, reddish-brown; coupled with naphthionic acid, an orange-red *compound*; and coupled with 1 : 4-naphtholsulphonic acid, a red *compound*. W. G.

Aromatic Telluretine Compounds. III. (Conclusion). KARL LEDERER (*Ber.*, 1915, **48**, 1944—1949. Compare A., 1913, i, 615, 724, 1182).—Some diaryl tellurides have been condensed with more halogeno-acids and esters, and some triaryltelluronium picrates have been prepared.

A mixture of diphenyl telluride and ethyl iodoacetate deposited, when exposed to light for a few days, garnet-red crystals of diphenyltelluronium iodide (from the free iodine), followed later by *ethyl diphenyltelluretine iodide* [*iododiphenyltelluriacetate*],

$$TePh_2I\cdot CH_2\cdot CO_2Et,$$

m. p. 110° (decomp.).

A solution of diphenyl telluride in α-bromopropionic acid was warmed at 60° for some time, and then diluted with ether, when

diphenyl-α-propionyltelluretine bromide [*α-bromodiphenyltelluripropionic acid*], $TePh_2Br\cdot CHMe\cdot CO_2H$, was precipitated, as a white powder, m. p. about 98°. Similarly, α-bromobutyric acid gave *diphenyl-α-butyryltelluretine bromide* [*α-bromodiphenyltelluributyric acid*], $TePh_2Br\cdot CHEt\cdot CO_2H$, m. p. 84—85°, whilst ethyl α-bromobutyrate yielded the corresponding *ethyl* ester, an amorphous substance, m. p. 142—143°, and ethyl α-bromo*iso*butyrate formed *ethyl diphenyl-α-*iso*butyryltelluretine bromide* [*α-bromodiphenyltelluri*iso*butyrate*], $TePh_2Br\cdot CMe_2\cdot CO_2Et$, m. p. about 130°.

A solution of di-*p*-tolyl telluride in methyl bromoacetate gradually deposited the *compound* $(C_7H_7)_2TeBr\cdot CH_2\cdot CO_2Me,CH_2Br\cdot CO_2Me$, m. p. 68°, from which the free *methyl di-*p*-tolyltelluretine bromide* [*bromodi-*p*-tolyltelluriacetate*] was obtained by repeated crystallisation from chloroform and ether, in aggregates of small prisms, m. p. 92—93°. The corresponding *ethyl* ester had m. p. 102—103°.

*Di-*o*-tolylmethyltelluronium chloride*, $(C_7H_7)_2TeMeCl$, was obtained by boiling the corresponding iodide with silver chloride and water. It crystallised from water in four-sided plates, with $2H_2O$, m. p. 93°, and again at 148°, and from chloroform with $\frac{1}{2}CHCl_3$, m. p. 155—156°.

Triphenyltelluronium hydroxide, $TePh_3\cdot OH$, was obtained by boiling the iodide with silver oxide and water, as an alkaline resin which formed a *picrate*, broad, yellow needles, m. p. 160°. *Tri-*p*-tolyltelluronium hydroxide*, a resin, m. p. about 110°, also formed a *picrate*, long prisms, m. p. 194—195°, whilst the resinous *tri-*o*-tolyltelluronium hydroxide* yielded a *picrate*, long, yellow prisms, m. p. 182°, a *chloride*, stout columns, m. p. 175—176°, and a *bromide*, m. p. 197—198°. J. C. W.

Some New Oxidation Derivatives of Cholesterol. St. Minovici and (Mme.) Th. Zenovici-Eremie (*Bull. Sci. Acad. Roumaine*, 1915, **4**, 194—205. Compare Minovici and Vlahuta, A., 1912, i, 697).—The authors have oxidised cholesterol with hydrogen peroxide under varying conditions, and have obtained five different compounds, to which they have been unable to assign any definite constitution.

When 10 grams of cholesterol were dissolved in 200 c.c. of glacial acetic acid on a water-bath, and a mixture of 50 grams of hydrogen peroxide in 100 c.c. of sulphuric acid (20%) slowly added, and the mixture slowly boiled for two hours, a clear, oily liquid was obtained which, when separated and washed with water, solidified to white floccula. These, when crystallised from acetone and water, gave a *compound*, $C_{24}H_{40}O_4$, acicular needles, m. p. 160°; $[\alpha]_D^{20}$ +41·47°. Submitted to Salkowski's reaction for cholesterol, the compound gave a colourless chloroform solution, the acid being coloured orange-yellow. In the Liebermann-Burchard reaction no play of colours was obtained, but only a deep violet-red coloration. The compound did not give Lifschutz's reaction for oxycholesterol. The substance contains no hydroxyl, phenolic, or ketonic group, and is not an ozonide or a peroxide.

It is very probably a lactone, and contains an acetyl group. It does not unite with bromine. When warmed with hydrobromic acid, it yields a *compound*, $C_{12}H_{23}Br$, m. p. 130°, and with hydrochloric acid a *compound*, $C_{12}H_{23}Cl$, m. p. 150°. The mother liquors from the compound, $C_{24}H_{40}O_4$, gave an oily substance, which resinified on contact with air, and after purification the *compound* was obtained as a yellow powder. The substance is slightly acid in character, and is soluble in alkalis, and gives a *silver* salt. It is probably a resin acid, having the composition $C_8H_{10}O_4$.

If in the original oxidation of the cholesterol an excess of hydrogen peroxide was used, an amorphous compound was obtained which was not characterised. If the original proportion of hydrogen peroxide was used, but added in larger portions at a time, a *compound* was obtained in white, lamellar crystals, m. p. 200°.

By slowly adding 20% sulphuric acid alone to a solution of cholesterol in gently boiling acetic acid, on cooling a crystalline *compound*, m. p. 110°—111°, was obtained. It was not cholesteryl acetate, since it was not decomposed by boiling with alcohol or water. It differed from cholestanyl acetate in that with phosphorus pentachloride it gave a crystalline *chloro-compound*, m. p. 95—97°, and with bromine in carbon disulphide a crystalline *bromo-derivative*, m. p. 116—118°. W. G.

Sitosterol and Stigmasterol. A. HEIDUSCHKA and H. W. GLOTH (*Arch. Pharm.*, 1915, **253**, 415—426).—After a brief summary of the work of Burian, Windaus, Ritter, Pickard and Yates, and Jaeger on these two sterols, the following new derivatives are described. *Sitosteryl salicylate*, $C_{27}H_{45}O{\cdot}CO{\cdot}C_6H_4{\cdot}OH$, has m. p. 147°, and separates from ether and alcohol in colourless, gelatinous flocks, which ultimately become crystalline. *Sitosteryl phenylcarbamate*, $C_{34}H_{51}O_2N$, forms crystals, m. p. 174°. By direct treatment with an excess of bromine, sitosterol yields *decabromositosterol*, $C_{27}H_{36}OBr_{10}$, a brown powder, m. p. about 185°, and *octabromositosterol*, $C_{27}H_{38}OBr_8$, a yellow powder, m. p. about 120°, the former of which is almost insoluble in alcohol.

Just as Windaus converted cholesterol, by oxidising its dibromide with acidified permanganate and debrominating the product by zinc and acetic acid, into cholestenone, so has sitosterol been now converted into *sitostenone*, $C_{27}H_{44}O$, crystals, m. p. 82°, which forms a *semicarbazone*, crystals, m. p. 254° (decomp.), sintering at 243°.

Stigmasterol forms a *palmitate*, $C_{30}H_{49}O{\cdot}CO{\cdot}C_{15}H_{31}$, silky crystals, m. p. 99°, *stearate*, crystals, m. p. 101°, *oleate*, colourless crystals, m. p. 44°, *salicylate*, colourless needles, m. p. 175°, and *cinnamate*, colourless crystals, m. p. 155°. By the oxidation of stigmasterol tetrabromide and debromination of the product a crystalline *substance*, m. p. 140°, was obtained, which did not exhibit the properties of a ketone. C. S.

The Substituted Benzoylbenzoic Acids. ALICE HOFMANN (*Monatsh.*, 1915, **36**, 805—824).—The author brings forward

further experimental proof of the fact that the presence of halogen substituents in phthalic anhydride facilitates the condensation of the latter with benzene derivatives.

When 3:6-dichlorophthalic anhydride is heated with dichlorobenzene and a little aluminium chloride at 200°, some hydrogen chloride is eliminated, and there is also produced 3:6:2′:5-*tetrachlorobenzoylbenzoic acid*, needles, m. p. 205—207°, which on heating at 140° with sulphuric acid is converted into 1:4:5:8-tetrachloroanthraquinone (compare Schilling, A., 1913, i, 493). During this condensation the acid undergoes slight concurrent decomposition into dichlorobenzene and 3:6-dichlorophthalic acid, the latter being observed as a sublimate of the anhydride. The tetrachlorobenzoylbenzoic acid was converted by thionyl chloride into the acid *chloride*, which on treatment with methyl alcohol yielded the *methyl* ester, needles, m. p. 145—148°, a second modification of this ester, m. p. 172°, being obtained by the interaction of the acid and the alcohol in the presence of a little sulphuric acid; the former modification (termed the *pseudo*-form) could be converted into the latter (the "normal" form) by boiling with methyl alcohol and a little sulphuric acid.

Tetrachlorophthalic anhydride and chlorobenzene reacted at 140° in the presence of a little aluminium chloride, producing *pentachlorobenzoylbenzoic acid*, m. p. 165°, which resembled the above tetrachloro- analogue in giving a non-crystalline "pseudo" *methyl* ester when the acid chloride was treated with the alcohol, and an amorphous "normal" ester when esterified directly by methyl alcohol in the presence of sulphuric acid. When heated at 140° with sulphuric acid, pentachlorobenzoylbenzoic acid yielded pentachloroanthraquinone.

The condensation of tetrachlorophthalic anhydride and dichlorobenzene in the presence of aluminium chloride at 220° gave *hexachlorobenzoylbenzoic acid*, colourless crystals, m. p. 238—239°, which, like the preceding acids, could be converted through the *chloride*, m. p. 181—184°, into a "pseudo" *methyl* ester, m. p. 180—182°, and by the usual process of esterification into an amorphous "normal" *methyl* ester. It also underwent intramolecular condensation when heated with sulphuric acid, yielding hexachloroanthraquinone, pale yellow needles, m. p. 298°.

In the usual manner, tetrachlorophthalic anhydride and nitrobenzene condensed together, giving *tetrachloronitrobenzoylbenzoic acid*, colourless crystals, m. p. 242—245°, the acid *chloride* (colourless crystals) of which was converted by methyl alcohol into an amorphous *methyl* ester.

By the addition of bromine to a heated mixture of phthalic acid and fuming sulphuric acid, there was obtained tetrabromophthalic acid, yellow crystals, m. p. 268°, which underwent condensation with benzene in the presence of aluminium chloride, giving *tetrabromobenzoylbenzoic acid*, m. p. 230—232°; the *methyl* ester, platelets, m. p. 108—111°, when heated with sulphuric acid in the usual way, apparently gives rise to a bromoanthraquinonesulphonic acid, the tetrabromoanthraquinone presumably being less resistant

than 1:2:3:4-tetrachloroanthraquinone towards sulphuric acid; the free acid, however, when carefully treated with sulphuric acid, may be made to yield *tetrabromoanthraquinone*, orange-red needles, m. p. 200—202° (in a closed tube).

With bromobenzene, tetrabromophthalic anhydride undergoes condensation, producing *pentabromobenzoylbenzoic acid*, m. p. 228—230°, which yields an oily "normal" *methyl* ester and an amorphous "pseudo" modification, m. p. 178—183°, and can also be made to undergo further condensation to pentabromoanthraquinone, m. p. 230—240°, the yield, however, being poor.

Tetrabromophthalic anhydride and dibromobenzene interacted under the usual conditions, producing hexabromobenzoylbenzoic acid, m. p. 218—219°, from which was obtained, by heating with sulphuric acid, a small quantity of *hexabromoanthraquinone*, m. p. 280—285°.

The condensation of tetrabromophthalic anhydride and dichlorobenzene gave *tetrabromobenzoyldichlorobenzoic acid*, m. p. 240—245°. In a similar manner tetraiodophthalic anhydride and benzene gave *tetraiodobenzoylbenzoic acid*, microscopic yellow crystals, m. p. 230—231° (*sodium* salt, silver leaflets), from which it was found impossible to produce the corresponding tetraiodoanthraquinone. D. F. T.

Preparation of Sulphomethylbenzophenone-*o*-carboxylic [Sulphomethyl-*o*-benzoylbenzoic] Acids and Substitution Products. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 285700; from *J. Soc. Chem. Ind.*, 1915, **34**, 1135).—The chlorides of benzoic acid or its substitution products are condensed with *m*-xylene, the new substances are sulphonated, and the resulting *as*-dimethylbenzophenonesulphonic acids, having the sulphonic group in the xylene residue, are oxidised. The *o*-carboxylic acids which are thus obtained may be condensed to anthraquinone derivatives by means of concentrated sulphuric acid. J. C. W.

Preparation of Derivatives of 2-Hydroxy-3-naphthamide. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 284997; from *J. Soc. Chem. Ind.*, 1915, **34**, 1136).—The hydroxynaphthylamides of 2-hydroxy-3-naphthoic acid are obtained by condensing aminonaphthols with the haloids or with the acid itself in the presence of dehydrating agents. Whereas the anilide is only soluble in lime water, and even so only to a slight extent, the new amides dissolve readily in warm, dilute sodium carbonate. They are freely absorbed from such solutions by unmordanted cotton, which then acquires very intense, clear, fast shades with diazo-solutions. J. C. W.

Preparation of Hydroxytriarylmethanecarboxylic Acids. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 286433; from *J. Soc. Chem. Ind.*, 1915, **34**, 1135).—A mixture of an aromatic *o*-hydroxycarboxylic acid (2 mols.) and an aromatic aldehyde (1 mol.) is treated with zinc chloride and phosphoryl chloride, reaction being completed by warming at 70°. The phosphoryl

chloride is recovered by distillation under reduced pressure. *o*-Chlorobenzaldehyde and *o*-creosotic acid yield chlorodihydroxydimethyltriphenylmethanedicarboxylic acid. J. C. W.

Phenylfumaric Acid. G. KARL ALMSTRÖM (*Ber.*, 1915, **48**, 2009—2010).—A substance has been obtained in another connexion which must be regarded as phenylfumaric acid, but as it did not agree with Barisch's description (A., 1880, 43), the acid has been prepared by boiling phenylmaleic anhydride (Alexander, A., 1890, 1136) with 2*N*-sodium hydroxide. *Phenylfumaric acid*, $C_{10}H_8O_4$, separates from benzene as a felted mass of needles, m. p. 128—129°, and from water, in which it is very soluble, with $2H_2O$. It quickly reduces permanganate, and is easily converted into phenylmaleic anhydride by melting. J. C. W.

Preparation of Compounds of Phenolphthalein and Alkali Carbonates. A. VON SZTANKAY and C. GEYER (D. R.-P., 286020; from *J. Soc. Chem. Ind.*, 1915, **34**, 1167).—Concentrated solutions of the alkali carbonates are treated with phenolphthalein, either in solution or as a freshly prepared suspension in water, at the ordinary temperature. Compounds of the type $2C_{20}H_{14}O_4,6Na_2CO_3$ are formed. They are strongly alkaline, are stable only in aqueous solution, and the therapeutic doses are much smaller than is the case with the known alkali salts of phenolphthalein.

J. C. W.

The Synthesis of Certain Substituted Syringic Acids. MARSTON TAYLOR BOGERT and EDWARD PLAUT (*J. Amer. Chem. Soc.*, 1915, **37**, 2723—2733).—A record of the earlier part of an investigation of derivatives of syringic acid (4-hydroxy-3:5-dimethoxybenzoic acid).

Methyl bromogallate trimethyl ether, prepared by the action of bromine on methyl gallate trimethyl ether in acetic anhydride solution, was obtained for the first time in the solid state, prisms, m. p. 90° (corr.), b. p. 202°/16 mm. (compare Hamburg, A., 1899, i, 364).

Syringic acid was converted by the Fischer-Speier reaction into the methyl ester (Graebe and Martz, A., 1903, i, 262; Bogert and Isham, A., 1914, i, 532), *ethyl* ester, crystals, m. p. 55·8° (corr.), and *iso*amyl ester, needles, m. p. 101° (corr.). On acetylation at the ordinary temperature by acetic anhydride, the methyl ester was converted into its *acetyl* derivative, $OAc\cdot C_6H_2(OMe)_2\cdot CO_2Me$, crystals, m. p. 129° (corr.), whilst bromination in cold acetic anhydride gave *methyl 2-bromosyringate*,

$$OH\cdot C_6HBr(OMe)_2\cdot CO_2Me,$$

crystals, m. p. 89° (corr.), which was also obtained by partial demethylation of methyl bromogallate trimethyl ether by heating with hydrobromic acid. Syringic acid in cold acetic acid solution is converted by nitric acid into 4:5-*dinitropyrogallol*-1:3-*dimethyl ether*, pale yellow crystals, m. p. 154° (corr.), the change being analogous to that undergone by trimethylgallic acid, but in solution in acetic anhydride at −5° methyl syringate undergoes nitration to *methyl 2-nitrosyringate*, $OH\cdot C_6H(OMe)_2(NO_2)\cdot CO_2Me$, pale

yellow crystals, m. p. 68·3° (corr.), which can also be obtained by heating methyl nitrogallate trimethyl ether with hydrobromic acid. *Ethyl 2-nitrosyringate*, almost colourless, silky needles, m. p. 74° (corr.), was prepared in an analogous manner to the methyl ester. The latter substance was reduced by tin and hydrochloric acid to *methyl 2-aminosyringate*, $OH\cdot C_6H(OMe)_2(NH_2)\cdot CO_2Me$, colourless crystals, m. p. 110° (corr.), which gradually darkens in the air; *hydrochloride*, needles, m. p. 192° (corr.); *diacetyl* derivative, large crystals, m. p. 139·9° (corr.). By diazotisation in diluted sulphuric acid solution and subsequently heating at 100°, the methyl ester was converted into 2 : 4-*dihydroxy*-3 : 5-*dimethoxybenzoic acid*, $C_6H(OH)_2(OMe)_2\cdot CO_2H$, pale yellow crystals, m. p. 165° (decomp.); *diacetyl* derivative, crystals, decomp. at 162°. In a preliminary experiment, in which the product from the thermal decomposition of the dihydroxydimethoxy-acid was recrystallised from alcohol and subsequently treated with methyl sulphate and sodium hydroxide solution, there was obtained a *substance*, glassy needles, m. p. 89° (corr.), possibly apionol tetramethyl ether.

D. F. T.

Derivatives of Methylvanillin, and a New Condensation Product. B. L. VANZETTI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 467—470. Compare Körner and Vanzetti, A., 1912, i, 352; Fritsch, A., 1904, i, 94).—Veratrylic acid [3 : 4 : 3′ : 4′-tetramethoxybenzilic acid] cannot readily be obtained by transposition or oxidation of the corresponding ketonic compounds according to the schemes, $\cdot CH(OH)\cdot CO\cdot \longrightarrow >C(OH)\cdot CO_2H$ and $\cdot CO\cdot CO\cdot \longrightarrow >C(OH)\cdot CO_2H$, although in other cases these changes are almost quantitative. Thus, whilst benzoin is transformed directly into benzilic acid by means of a current of air in presence of alkali in the hot, veratroin merely undergoes quantitative oxidation to veratril under these conditions. Veratrylic acid may be obtained moderately pure (m. p. about 68°), but by no means in quantitative yield by the prolonged action of alcoholic potassium hydroxide on veratril in the hot.

Another starting point for preparing veratrylic acid is veratrophenone (3 : 4 : 3′ : 4′-tetramethoxybenzophenone), m. p. 144·5°, which may be obtained by converting veratric acid into veratroyl chloride, m. p. 70—71°, and treating the latter with veratrole (1 mol.) in presence of aluminium chloride. The further stages are represented by the scheme,

$$\begin{smallmatrix}R\\R\end{smallmatrix}\!>CO + MgMeI \longrightarrow \begin{smallmatrix}R\\R\end{smallmatrix}\!>C<\!\begin{smallmatrix}Me\\O\cdot MgI\end{smallmatrix} \longrightarrow \begin{smallmatrix}R\\R\end{smallmatrix}\!>C<\!\begin{smallmatrix}Me\\OH\end{smallmatrix}\text{(m. p. 95—96°)}$$

$$\longrightarrow \begin{smallmatrix}R\\R\end{smallmatrix}\!>C{:}CH_2,\text{ which, on oxidation, } \longrightarrow \begin{smallmatrix}R\\R\end{smallmatrix}\!>C<\!\begin{smallmatrix}OH\\CO_2H\end{smallmatrix}.$$

The various compounds obtained in this way, which is not very convenient for preparing the acid, are to be described elsewhere.

Fusion of veratril with potassium hydroxide also gives poor yields of veratrylic acid, although high yields of benzilic and anisylic acids and somewhat lower ones of piperonylic acid are obtainable in this way. The yield of veratrylic acid varies considerably with

the temperature of the fusion, and in some cases more complicated transformations occur, the mass becoming dark coloured and resinous. Treatment of the resin with various solvents yields an orange-yellow *compound*, m. p. 198°, and crystallisation of this from acetic acid gives shining, brownish-red needles, which at 110—120° are converted into the orange-yellow compound. With cold concentrated sulphuric acid, the latter gives a greenish-blue coloration, which changes in a few minutes to a red coloration; subsequent dilution, either spontaneous or otherwise, produces a reddish turbidity owing to precipitation of the compound in the form of powder. Except that the proportion of hydrogen is rather low, the composition of this compound approximates closely to that of veratril. The transformation which the veratril undergoes in the formation of this compound appears to be analogous to the thermal decomposition of benzilic acid which is now under investigation. T. H. P.

Preparation of Tetrachlorobenzaldehyde and New Colouring Matters therefrom. L. CASSELLA & Co. (Eng. Pat., 1915, 13970; from *J. Soc. Chem. Ind.*, 1915, **34**, 1243).—Tetrachlorobenzaldehyde is obtained as a white powder, which crystallises from ether in colourless needles, m. p. 97—98°, by dissolving tetrachlorobenzylidene chloride in six parts of concentrated sulphuric acid at 90° and pouring into iced water. The above solution in sulphuric acid or tetrachlorobenzaldehyde itself condenses with *o*-hydroxycarboxylic acids, such as *o*-cresotic acid, to give leuco-compounds, which on oxidation with sodium nitrite in sulphuric acid, nitric acid, nitro-compounds, or fuming sulphuric acid, yield valuable new dyes of the triphenylmethane series. These dyes surpass in intensity and fastness other known dyes of a similar character, and are distinguished by their bright greenish-blue shade. G. F. M.

Semicarbazones. V. Semicarbazones of Benzaldehyde and Some of its Substitution Products. JAMES ALEXANDER RUSSELL HENDERSON and ISIDOR MORRIS HEILBRON (T., 1915, **107**, 1740—1752. Compare T., 1912, **101**, 1482; 1913, **103**, 377, 1504; 1914, **105**, 2892).—The absorption spectra and the power to form salts with dry hydrogen chloride of various semicarbazones have been investigated.

Semicarbazones with hydroxy- or methoxy-groups in the nucleus are found to absorb two molecular proportions of hydrogen chloride, giving yellow to red salts. If the nucleus contains a strongly negative substituent, such as chlorine or nitroxyl, the semicarbazone only absorbs one proportion of the gas, forming a practically colourless salt. The acetylation or benzoylation of salicylaldehyde has no influence on the additive capacity of the semicarbazone, but the *p*-nitrobenzoyl derivative gives a semicarbazone which only absorbs 1 mol. of hydrogen chloride. No definite result could be obtained in the case of *p*-dimethylaminobenzaldehydesemicarbazone, which absorbed nearly 4HCl, and *p*-tolualdehydesemicarbazone, which combined with nearly 2HCl.

Some semicarbazones were observed to form labile, more coloured modifications, which are probably the isomerides of the stable products finally obtained after repeated crystallisations.

The absorption spectra were examined in solutions in alcohol, alcoholic sodium ethoxide, and concentrated sulphuric acid. With the exception of the *p*-dimethylamino- and *p*-nitro-compounds, the semicarbazones show a band in $N/10000$-alcoholic solution at about $1/\lambda\ 3500$. The addition of sodium ethoxide to the solutions of the hydroxy-, but not methoxy-compounds displaces the band towards the red. Semicarbazones containing hydroxyl or methoxyl in the ortho-position show a band in concentrated sulphuric acid at about $1/\lambda 2600$ which is not exhibited by the others.

p-Tolualdehydesemicarbazone gave a yellow *hydrochloride*, $C_9H_{11}ON_3,1\frac{1}{2}HCl$, which rapidly decomposed in the air.

Salicylaldehydesemicarbazone gave an unstable, yellow *dihydrochloride* and a straw-yellow, fairly stable *sulphate*, $C_8H_9O_2N_3,H_2SO_4$, decomp. 150°. *o-Methoxybenzaldehydesemicarbazone*, colourless needles, m. p. 215° (decomp.), formed a dark orange, fairly stable *dihydrochloride*. *p*-Hydroxybenzaldehydesemicarbazone, when first formed, contained a yellow admixture, probably the labile isomeride, and it yielded an unstable, yellow *dihydrochloride* and a yellow *sulphate*. *p*-Methoxybenzaldehydesemicarbazone was obtained in a labile form, small, transparent, yellow prisms, m. p. 168°, very soluble in acetone, and the usual colourless form, m. p. 209° (decomp.). It gave an unstable, orange-yellow *dihydrochloride* and a mustard-yellow, stable *sulphate*, decomp. 152°.

Vanillinsemicarbazone formed a very unstable, orange-yellow *dihydrochloride*. Veratraldehydesemicarbazone yielded an unstable, orange *dihydrochloride*, decomp. 130°. *Piperonalsemicarbazone dihydrochloride*, deep orange-red, lost hydrogen chloride in the air. *2-Hydroxy-*m*-methoxybenzaldehydesemicarbazone*, $C_9H_{11}O_3N_3$, colourless needles, m. p. 225° (decomp.), gave an unstable, yellow *dihydrochloride*, m. p. 158° (decomp.). *2:3-Dimethoxybenzaldehydesemicarbazone*, white needles, m. p. 231° (decomp.), yielded a dirty yellow *dihydrochloride*.

The chlorobenzaldehydesemicarbazones gave the following unstable *hydrochlorides*: *ortho*, cream coloured, decomp. 203°; *meta*, colourless, decomp. 198°; *para*, pale yellow, decomp. 182°. The nitrobenzaldehydesemicarbazones yielded the following *hydrochlorides*: *ortho*, cream coloured, unstable, decomp. 212°; *meta*, cream coloured, unstable, decomp. 222°; *para*, pink, stable, not decomposed at 275°.

o-*Acetoxybenzaldehydesemicarbazone*, $C_{10}H_{11}O_3N_3$, a colourless, granular powder, m. p. 167°, gave an unstable, dark yellow *dihydrochloride*. o-*Benzoyloxybenzaldehydesemicarbazone*, colourless needles, m. p. 195—196° (decomp.), formed a cream coloured, unstable *dihydrochloride*. 2-p-*Nitrobenzoyloxybenzaldehyde*, $C_{14}H_9O_5N$, was obtained by the action of the acyl chloride on salicylaldehyde in pyridine solution, in the form of pale yellow leaflets, m. p. 128°, which yielded the *semicarbazone*,

$$NO_2\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CH{:}N\cdot NH\cdot CO\cdot NH_2,$$

pale yellow needles, m. p. 218° (decomp.); *hydrochloride*, colourless and unstable.

p-Dimethylaminobenzaldehydesemicarbazone showed the same absorption band in alcohol as the *p*-hydroxy-compound did in alcoholic sodium ethoxide. When first formed, it was dark red, but the recrystallised substance was white, and the *hydrochloride*, 3—4HCl, was very unstable and greenish-blue. J. C. W.

Constitution of the Salts of Phenol-aldehydes. II. H. PAULY (*Ber.*, 1915, **48**, 2010—2018. Compare A., 1915, i, 689). —A continuation of the controversy with Hantzsch (A., 1915, i, 551, 1062). Hantzsch adheres to his quinonoid isomerism theories to explain the coloured salts of phenol-aldehydes, but Pauly maintains that all the problems connected with the manifold activities of the carbonyl group are best explained by valence-electron formulation.

The following salts are described: The sodium salts of salicylaldehyde, $C_7H_5O_2Na,C_7H_6O_2,\frac{1}{2}H_2O$ (Ettling, 1840), and
$$C_7H_6O_2,C_7H_5O_2Na$$
(Hantzsch, 1906), both of which are pure white; the *sodium* salt of *iso*vanillin, $C_8H_7O_3Na$, sulphur-yellow needles; and the *sodium* salt of bromo*iso*vanillin, $C_8H_6O_3BrNa$, a bright yellow, crystalline precipitate. *Bromo*iso*vanillin*, or probably 2-bromo-5-hydroxy-4-methoxybenzaldehyde, the product of the action of bromine dissolved in acetic acid on *iso*vanillin, forms snow-white needles, m. p. 208°. J. C. W.

Isomerism of the Oximes. VII. 5-Bromovanillinoxime, 5-Nitrovanillinoxime, and 6-Nitropiperonaloxime. OSCAR LISLE BRADY and FREDERICK PERCY DUNN (T., 1915, **107**, 1858—1862). —It has been found that certain negative substituents in the benzene ring seem to favour the existence of two isomeric oximes. The effect of introducing such groups into vanillinoxime has therefore been examined, for this contains groups, namely, methoxyl and hydroxyl, which inhibit the formation of a second isomeride. 5-Bromo- and 5-nitro-vanillinoximes could only be obtained in the *anti*-form, however, which shows that the negative groups do not counterbalance the effect exercised by the other groups. Unlike vanillinoxime, piperonaloxime can readily be obtained in the *syn*-form, and, therefore, it was expected that the 6-nitro-derivative would also exist in the two forms. Strange to say, it does not form a hydrochloride, so the two distinct modifications could not be characterised.

5-*Bromovanillinoxime*, $C_8H_8O_3NBr$, was obtained from the product of the direct bromination of vanillin in colourless needles, m. p. 179°. The position of the bromine atom was proved by converting the oxime, ultimately, into 5-bromo-4-hydroxy-3-methoxybenzoic acid (Robertson, T., 1908, **93**, 792). The oxime was first converted by boiling acetic anhydride into 5-*bromo*-4-*acetoxy*-3-*methoxybenzonitrile*, $C_{10}H_8O_3NBr$, colourless crystals, m. p. 110—111°, and this was hydrolysed by boiling with dilute

sodium hydroxide for a few minutes to *5-bromo-4-hydroxy-3-methoxybenzonitrile*, needles, m. p. 144° (*sodium* salt, shining plates), and then, on continuing the boiling, to the above acid. The oxime formed a *diacetate*, $C_{12}H_{12}O_5NBr$, a microcrystalline powder, m. p. 122°, and a *hydrochloride*, m. p. 175° (decomp.), from both of which the original oxime could be recovered.

5-Nitrovanillinoxime, as obtained from the aldehyde by means of hydroxylamine, had m. p. 216° (Vogl, A., 1899, i, 698, gave m. p. 200—201°), and formed a red *sodium* salt. It was converted into a *diacetate*, $C_{12}H_{12}O_7N_2$, a yellow, crystalline powder, m. p. 112°, and a *monoacetate*, orange needles, with $1H_2O$, m. p. 147°, the latter being obtained most conveniently by the action of acetyl chloride dissolved in pyridine. It also yielded a *hydrochloride*, m. p. 204° (decomp.), but all these derivatives gave the original oxime when suitably treated.

6-Nitropiperonaloxime was converted into the *acetate*, $C_{10}H_8O_6N_2$, yellow needles, m. p. 142°. J. C. W.

Chlorination Experiments with Antimony Pentachloride KARL STEINER (*Monatsh.*, 1915, **36**, 825—829. Compare Eckert and Steiner, A., 1915, i, 564, 565).—An extension of the earlier investigation.

When heated with antimony pentachloride, benzophenone gave hexachlorobenzene as the main product, together with a little *perchlorobenzophenone*, $CO(C_6Cl_5)_2$, colourless needles, m. p. 318°, and perchlorobenzoic acid. Benzil gave rise to hexachlorobenzene with a little perchlorobenzoic acid. 1 : 2-Naphthaquinone yielded tetrachlorophthalic acid and perchloronaphthaquinone.

Under similar treatment, benzoic acid and benzoyl chloride yielded hexachlorobenzene, together with a mixture of chlorinated benzoic acids, whilst phthalic acid gave a mixture of the same nature. With benzoylbenzoic acid the chief products were perchlorobenzoylbenzoic acid and 1 : 2 : 3 : 5 : 6 : 7 : 8-heptachloroanthraquinone accompanied by small quantities of tetrachlorophthalic acid and hexachlorobenzene.

By using a suitable solvent, such as tetrachloroethane, the action of the antimony pentachloride can be moderated, and with a 10% solution of anthraquinone in this liquid the chief product is 1 : 4 : 5 : 8-tetrachloroanthraquinone. D. F. T.

Indones. II. Synthesis of 3-Phenyl-2-methylindone. R. DE FAZI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 343—348. Compare A., 1915, i, 1063).—Similarly to 3-phenyl-2-ethylindone, 3-phenyl-2-methylindone (compare Rupe, Steiger, and Fiedler, A., 1914, i, 281) may be obtained by the action of cold, concentrated sulphuric acid on ethyl β-hydroxy-ββ-diphenyl-α-methylpropionate (Rupe, Steiger, and Fiedler, *loc. cit.*):

$$OH\cdot CPh_2\cdot CHMe\cdot CO_2Et \longrightarrow OH\cdot CPh_2\cdot CHMe\cdot CO_2H \longrightarrow$$

$$CPh_2{:}CMe\cdot CO_2H \longrightarrow C_6H_4{<}{}^{CPh}_{-CO}{>}CMe.$$

The *oxime* of *3-phenyl-2-methylindone*, $C_{16}H_{13}ON$, forms shining, yellowish-green prisms, m. p. 199—200°, and, in the cold, gives a blood-red coloration with concentrated sulphuric acid, and a ruby-red coloration with concentrated nitric acid; the semicarbazone forms orange-red, indented leaflets, m. p. 219—220° (Rupe, Steiger, and Fiedler, *loc. cit.*, gave m. p. 200—201°), and gives intense blue and cherry-red colorations in the cold with concentrated sulphuric and nitric acids respectively; the *semioxamazone*, $C_{18}H_{15}O_2N_3$, forms tufts of intensely yellow, shining needles, m. p. 203—205°, and gives blue and cherry-red colorations in the cold with concentrated sulphuric and nitric acids respectively.

The *semicarbazone* of *3-phenyl-2-ethylindone* (compare A., 1915, i, 1064), $C_{18}H_{17}ON_3$, forms tufts of shining, orange-yellow needles, m. p. 198—199°, and gives cherry-red and intense blue colorations in the cold with concentrated nitric and sulphuric acids respectively. T. H. P.

Quinhydrones. WILHELM SIEGMUND (*J. pr. Chem.*, 1915, [ii], **92**, 342—370. Compare A., 1909, i, 109; 1911, i, 654).—After a discussion of the various constitutions proposed for the quinhydrones, the author decides in favour of the suggestion of Willstätter and Piccard (A., 1908, i, 475), who apply to these compounds a formula of the type

$$C_6H_5{\cdot}O \cdots H \cdots O{=}C_6H_4{=}O \cdots H \cdots O{\cdot}C_6H_5,$$

the undulating lines indicating partial valencies. This view of the structure is considered to be in good accord with the tendency of the quinone constituent of some "mixed" quinhydrones (that is, quinhydrones in which the quinone and the phenol are not derived from the same parent hydrocarbon) to remove hydroxylic hydrogen atoms from the accompanying phenol and so to effect oxidation to the true quinhydrone corresponding with the phenol.

The following quinhydrone compounds are described, the general method of preparation being to mix a light petroleum solution of the quinone with an ethereal solution of the phenol, and to allow the mixture to crystallise. From thymoquinone and quinol, the *compound*, $2C_{10}H_{12}O_2,3C_6H_6O_2$, red needles, decomp. 137°; from thymoquinone and resorcinol an unstable, red *compound*, decomp. 43—45°, the proportion of resorcinol being between unimolecular and sesquimolecular; from thymoquinone and catechol a red, oily *compound*, $2C_{10}H_{12}O_2,3C_6H_6O_2$. *p*-Xyloquinone with quinol and catechol respectively gave red needles, m. p. 153—156°, and red monoclinic crystals, m. p. 87°; each of the molecular composition, $C_8H_8O_2,2C_6H_6O_2$. *m*-Xyloquinone in a similar manner with quinol and catechol gave isomeric compounds of the same composition, very deep red leaflets, m. p. 120—121°, and long, red needles, m. p. 44—45°, respectively. Likewise, *o*-xyloquinone with quinol and catechol gave similar *compounds*, deep red needles with a green lustre, m. p. 118°, and red needles, m. p. 60—62° respectively. Resorcinol formed no quinhydrone compounds with the xyloquinones.

Chlorobenzoquinone and quinol gave a *compound*,

$$2C_6H_3O_2Cl,3C_6H_4(OH)_2,$$

bronze-coloured crystals, m. p. 123—124° (compare Ling and Baker, T., 1893, **63**, 1314; Schmidlin, A., 1911, i, 727). *m*-Dichloro-, trichloro-, and tetrachloro-benzoquinone, when mixed with quinol, oxidised this substance to ordinary benzoquinone-quinol quinhydrone. Benzoquinone with gentisic acid, β-resorcyclic acid, and protocatechuic acid, gave rise respectively to very deep red needles of no definite m. p., red prisms of no definite m. p., and deep red crystals, m. p. 179—180°, the products being isomerides of the composition $C_6H_4O_2,2C_7H_6O_4$. Benzoquinone with orcinol gave deep red prisms of a *compound*, $C_6H_4O_2,C_7H_8O_2$, hydrated orcinol also giving red crystals of a *compound*,

$C_6H_4O_2,C_7H_8O_2,H_2O$.

With gallic acid and ethyl gallate, benzoquinone was converted into ordinary quinhydrone.

The results show that although there is no simple law ruling the composition of the quinhydrones, a considerable regularity exists in the influence exerted by various substituent groups. For the analysis of the above products the author made use of the titanium trichloride method (Knecht and Hibbert, A., 1911, ii, 76).

D. F. T.

The Action of the Three Isomeric Aminophenols on α-Naphthaquinone. EMIL GROSSMANN (*J. pr. Chem.*, 1915, [ii], **92**, 370—390).—The general method of procedure was to allow the naphthaquinone (2 mols.) to react with the aminophenol (1 mol.) in hot alcoholic solution, the resulting compound being formed by the condensation of one molecule of each, the second molecule of naphthaquinone serving as the necessary oxidising agent.

The condensation of *p*-aminophenol and naphthaquinone gave 2-p-*hydroxyanilino-α-naphthaquinone*, $C_{10}H_5O_2{\cdot}NH{\cdot}C_6H_4{\cdot}OH$, red needles, m. p. 225°, which was reducible to a colourless compound. The formation of the condensation product was examined from a quantitative point of view, and the mechanism was demonstrated to be as described above, the second molecule of naphthaquinone being reduced to the corresponding quinol. The product gave cherry-red solutions in concentrated acids, and blue solutions in alkalis; it possessed only feeble acidic properties, and the preparation of the corresponding phenoxides miscarried, with the possible exception of the *potassium* derivative, in the attempt to produce which an unstable, blue, amorphous powder was obtained. Methylation with methyl sulphate also failed to give a satisfactory result, the product consisting of a mixture of red needles and deep violet, capillary needles. The *methyl ether* of 2-*p*-hydroxyanilino-α-naphthaquinone, $C_{10}H_5O_2{\cdot}NH{\cdot}C_6H_4{\cdot}OMe$, was therefore prepared in the usual manner from naphthaquinone and *p*-anisidine in alcoholic solution containing a little acetic acid, the product forming fiery red needles, m. p. 158°; the corresponding *ethyl ether*, $C_{10}H_5O_2{\cdot}NH{\cdot}C_6H_4{\cdot}OEt$, obtained from naphthaquinone and *p*-phenetidine, consisted of deep red needles, m. p. 264°; *acetyl* derivative, $C_{10}H_5O_2{\cdot}NAc{\cdot}C_6H_4{\cdot}OEt$, a deep raspberry-red, microcrystalline powder, m. p. 175°. When treated in the cold with

acetic anhydride and concentrated sulphuric acid, *p*-hydroxyanilino-α-naphthaquinone was converted into a *diacetyl* derivative, $C_{10}H_5O_2\cdot NAc\cdot C_6H_4\cdot OAc$, red, prismatic needles, m. p. 170°, and with benzoyl chloride and pyridine it gave a benzoyl derivative,

$$C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot OBz,$$

deep orange-red needles, m. p. 210°.

2-m-*Hydroxyanilino-α-naphthaquinone* was prepared in an analogous manner to its para-isomeride, and was found to form deep violet needles, m. p. 242°, soluble in potassium hydroxide to an azure-blue solution, and in sulphuric or hydrochloric acid to a cherry-red solution; *benzoyl* derivative, deep red, prismatic needles, m. p. 208°. The *methyl* and *ethyl ethers* were obtained by effecting the condensation of naphthaquinone with *m*-anisidine and *m*-phenetidine, the compounds forming long, red needles, m. p. 172°, and deep red needles, m. p. 195°, respectively.

2-o-*Hydroxyanilino-α-naphthaquinone*, prepared from naphthaquinone and *o*-aminophenol, is an almost black substance with very little tendency to crystallisation; it was obtained in brown flocks, m. p. 175°, and as a chocolate-brown, microcrystalline powder, m. p. 205°. The corresponding *methyl* and *ethyl ethers*, obtained by effecting a similar condensation between naphthaquinone and *o*-anisidine and *o*-phenetidine, formed deep red needles, m. p. 146°, and fiery red needles, m. p. 152°, respectively. D. F. T.

Preparation of Chloroanthraquinones. AKTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (Eng. Pat., 1915, 5182; from *J. Soc. Chem. Ind.*, 1915, **34**, 1203).—Hydroxyl groups in anthraquinone derivatives are replaced by chlorine, without affecting the ketonic groups or the hydrogen atoms of the nucleus, by the action of the chlorine compounds of phosphorus. Thus, for example, 1-hydroxyanthraquinone, when treated in nitrobenzene solution at 150° with phosphorus pentachloride, and boiled for three hours under a reflux, gives, after removing the nitrobenzene by steam distillation, 1-chloroanthraquinone, which is recrystallised from glacial acetic acid. G. F. M.

Preparation of Anthraquinone Derivatives [Mercaptans]. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (Eng. Pat., 8254, June, 1915; from *J. Soc. Chem. Ind.*, 1915, **34**, 1136).—α-Hydroxy- or α-amino-derivatives of anthraquinone are heated with an alkaline sulphide, with or without added sulphur, at 140—150°, when the hydrogen atom in the ortho-position with regard to the hydroxyl or amino-group is replaced by the thiol group. The products are valuable dyes or intermediate substances. J. C. W.

Preparation of Dianthraquinone Oxides. AKTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (Eng. Pat., 24347; 1914, Dec.; from *J. Soc. Chem. Ind.*, 1915, **34**, 1135).—1-Nitroanthraquinone, or its substituted products, yield 1 : 1′-dianthraquinone oxide or its derivatives when heated with an acid-fixing substance, such as an alkali carbonate, in an indifferent solvent of the aromatic series.

J. C. W.

Preparation of New Phenanthraquinone Dyes. E. R. WATSON and K. C. MUKHERJEE (Eng. Pat., 9311, June, 1915; from *J. Soc. Chem. Ind.*, 1915, **34**, 1136).—Bromo- or bromonitro-derivatives of phenanthraquinone are condensed with amines of the benzene or naphthalene series, giving dyes which colour chrome-mordanted or unmordanted wool fast dark blue, violet, or greenish-blue shades. The fastness to light is improved by sulphonation. Example: bromo-2-nitrophenanthraquinone (100 parts) is boiled with aniline (1000) and copper powder (25) for two hours, when the hot liquid is filtered into an excess of dilute hydrochloric acid, the 2-nitroanilinophenanthraquinone being precipitated. J. C. W.

*iso***Pulegolphosphonic Acid.** FRANCIS H. DODGE (*J. Amer. Chem. Soc.*, 1915, **37**, 2756—2761).—A re-investigation of the compound originally termed citronellal-phosphoric acid, and now designated *iso*pulegolphosphonic acid, which the author obtained earlier (A., 1891, 286) from citronellal and phosphoric oxide in the presence of a little water. The substance is a monobasic acid, m. p. 181—182°, which crystallises in large, monoclinic plates ($a:b:c = 1\cdot9828:1:1\cdot9745$, $\beta = 57\cdot83°$); *potassium* salt, $C_{10}H_{18}PO_4K,3H_2O$, large plates; *sodium* salt, plates; *magnesium* salt, plates; *calcium* salt; *silver* salt. When cautiously heated, the sodium salt decomposes with formation of *iso*pulegol. In spite of its monobasic character, the acid is regarded as a phosphinic acid of the structure $PRO(OH)_2$, the constitution of the radicle R being uncertain.

The formation of this acid shows no promise of providing a reaction for the detection of citronellal in essential oils.

D. F. T.

Constituents of Oil of Cassia. FRANCIS D. DODGE and ALFRED E. SHERNDAL (*J. Ind. Eng. Chem.*, 1915, **7**, 1055—1056).—The oil of *Cinnamomum cassia* contains at least 0·5% soluble in dilute alkali, from which by acidification and steam distillation about 25% of its weight of salicylaldehyde was isolated. The rest of the alkali soluble portion consisted of coumarin (60%), cinnamic acid (8—10%), and small amounts of benzoic and salicylic acids, and an unidentified, liquid, volatile acid. G. F. M.

Action of Xanthydrol with some Amides and Amines. W. ADRIANI (*Rec. trav. chim.*, 1915, **37**, 180—210. Compare Fosse, A., 1914, i, 859).—An examination of the behaviour of xanthydrol towards substituted carbamides and towards aromatic amines and their derivatives substituted in the nucleus or in the amino-group.

Monosubstituted carbamides give monoxanthyl derivatives with xanthydrol in alcoholic solution in the presence of acetic acid. The author has prepared *xanthylmethylcarbamide*, $C_{15}H_{14}O_2N_2$, m. p. about 230°, phenylxanthylcarbamide, m. p. 225° (compare Fosse, *loc. cit.*), o-*tolylxanthylcarbamide*, $C_{21}H_{18}O_2N_2$, m. p. 228°, p-*tolylxanthylcarbamide*, and *β-naphthylxanthylcarbamide*, $C_{24}H_{18}O_2N_2$.

Of the disubstituted carbamides, the symmetrical derivatives do not form xanthyl compounds, whilst the unsymmetric derivatives give monoxanthyl compounds, such as *diphenylxanthylcarbamide*,

$C_{26}H_{20}O_2N_2$, m. p. 179—180°, and *xanthyl*-as-*dimethylcarbamide*, $C_{16}H_{16}O_2N_2$, m. p. 225°, have been prepared. *s*-Diphenylcarbamide and *s*-dimethylcarbamide were recovered unchanged.

With aniline in the presence of a small amount of acetic acid in alcoholic solution xanthydrol gave *dixanthylaniline*, $C_{32}H_{23}O_2N$, together with a small amount of *xanthylaniline*, $C_{19}H_{15}ON$, m. p. 185·5—187°. The latter compound was also obtained by the action of xanthydrol on aniline hydrochloride under the usual conditions or by the action of xanthydrol on aniline in the presence of a large excess of acetic acid.

The three toluidines gave dixanthyl derivatives. Thus *dixanthyl*-o-*toluidine*, $C_{33}H_{25}O_2N$, *dixanthyl*-m-*toluidine*, and *dixanthyl*-p-*toluidine* were prepared. Of the xylidines examined, *m*-4-xylidine gave a *dixanthyl*, $C_{34}H_{27}O_2N$, whilst *m*-2-xylidine only gave a *monoxanthyl* derivative, m. p. 170·5°. The three nitroanilines all gave monoxanthyl derivatives, *xanthyl*-o-*nitroaniline*, $C_{19}H_{14}O_3N_2$, *xanthyl*-m-*nitroaniline*, and *xanthyl*-p-*nitroaniline* being prepared. Neither 2:4-dinitroaniline nor picramide gave any xanthyl derivative.

Of the anilines substituted in the amino-group, methylaniline gave *dixanthylmethylaniline*, $C_{33}H_{25}O_2N$, and dimethylaniline gave xanthyldimethylaniline (compare Fosse, *loc. cit.*). Diphenylamine yielded *xanthyldiphenylamine*, $C_{25}H_{19}ON$, and acetanilide gave a small amount of xanthylaniline.

From the naphthylamines there were obtained respectively *dixanthyl-α-naphthylamine*, $C_{36}H_{25}O_2N$, and *dixanthyl-β-naphthylamine*.

As an example of substances in which the nitrogen is linked to a strongly negative group, benzamide and methylnitroamine were chosen. The former gave *xanthylbenzamide*, $C_{20}H_{15}O_2N$, m. p. 218°, and the latter gave *xanthylmethylnitroamine*, $C_{14}H_{12}O_3N_2$, m. p. 117·5°.

The behaviour of these compounds towards hydrochloric acid was then examined, to see if xanthyl chloride was liberated, as indicated by an intense yellow coloration. Of the substances described above, all gave a yellow coloration except xanthylaniline, xanthylxylidine, derived from *m*-2-xylidine, xanthyldimethylaniline, xanthyldiphenylamine, and dixanthyl-α-naphthylamine. Dixanthylaniline gave the yellow coloration indicative of the formation of xanthyl chloride, but at the same time a precipitate of xanthylaniline, m. p. 185·5—187°, was obtained.

These results indicate that in xanthylaniline, xanthyldimethylaniline, and xanthyldiphenylamine, the xanthyl group, and in dixanthylaniline and dixanthylmethylaniline, one of the xanthyl groups is attached to the benzene ring, and the other to the amino-nitrogen. In the case of the monosubstituted carbamides and the asymmetric disubstituted carbamides, the xanthyl group has entered the second amide group thus: $NHMe\cdot CO\cdot NH\cdot C_{13}H_9O$ and $NMe_2\cdot CO\cdot NH\cdot C_{13}H_9O$. In the case of the derivatives from the three toluidines and *m*-4-xylidine, one of the xanthyl groups is attached to the nitrogen atom and the other to the benzene ring.

The evidence in the case of the three xanthylnitroanilines is not clear, but the xanthyl group is possibly attached to the benzene ring. The two xanthyl groups in dixanthyl-α-naphthylamine are attached to carbon, whilst in the β-isomeride at least one of the xanthyl groups is attached to nitrogen. In xanthylbenzamide the xanthyl radicle is attached to nitrogen, and this is probably true of xanthylmethylnitroamine, since it gives the reaction for true nitroamines.

These colour reactions with hydrochloric acid are confirmed by the green fluorescence test with sulphuric acid. The above-mentioned exceptions do not give the green fluorescence characteristic of xanthydrol, whilst all the others do. The author considers that the general constitution of these xanthydrol derivatives is better represented by formula I than by formula II, bringing them into

(I.) (II.)

agreement with the accepted formula for xanthyl chloride.

W. G.

Process for Hydrogenating Unsaturated Substances. C. F. BOEHRINGER & SÖHNE (Eng. Pats., 1914, 21883 and 21948; from *J. Soc. Chem. Ind.*, 1915, **34**, 1225).—The unsaturated substance in aqueous or alcoholic solution or suspension is treated with hydrogen in presence of a suboxide of nickel, copper, iron, or cobalt as catalyst. Details of the hydrogenation of quinine hydrochloride, morphine, cinnamylcocaine, cinnamic acid, and aminoacetonitrile are given.

G. F. M.

Preparation of a Derivative of Thebaine. M. FREUND and E. SPEYER (D.R.-P. 286431; from *J. Soc. Chem. Ind.*, 1915, **34**, 1168).—A new *base*, $C_{20}H_{22}O_4N$, decomp. above 275°, is obtained by treating thebaine in acid solution with hydrogen peroxide or potassium dichromate.

J. C. W.

Action of Grignard's Reagent on Tertiary Pyrroles. K. HESS (*Ber.*, 1915, **48**, 1969—1974. Compare A., 1914, i, 725).—A reply to Oddo (A., 1914, i, 1142). Hess and Wissing obtained some 2-acyl-1-methylpyrroles by treating 1-methylpyrrole with magnesium ethyl bromide and then with acyl chlorides. They assumed that magnesium 1-methyl-2-pyrryl bromide was first formed, with the evolution of ethane. Oddo pointed out that 1-methylpyrrole does not react with the Grignard reagent, and assumed that Hess's base contained free pyrrole. The author now states that his base was pure, but that it certainly does not give ethane unless water is present. It must combine with the magnesium ethyl bromide, however, otherwise this would react with the acyl chloride to give a carbinol, which it does not. Moreover, the additive compound which it forms is unaffected by an acyl chloride until water is added, when the 2-acyl-1 methylpyrrole and ethane are produced.

An arrangement is described by which it is possible to determine whether ethane is liberated even when such reactions are carried out in a hygroscopic liquid like ether, and if so, to estimate it.

J. C. W.

Action of Derivatives of the Propane Series on Pyrrole. II. KURT HESS and HEINRICH FINK (*Ber.*, 1915, **48**, 1986—2005. Compare A., 1913, i, 1378).—The preparation of pyrroles substituted by derivatives of propane opens up the possibility of synthesising certain bases of the pyrrolidine series, such as hygrine, cuskhygrine, and tropine. A number of compounds of this nature have therefore been prepared.

An ethereal solution of epichlorohydrin was treated with potassiopyrrole, when two products were obtained, namely, *α-1-pyrrylpropylene βγ-oxide*, $C_4H_4N\cdot CH_2\cdot \underset{\diagdown O \diagup}{CH-CH_2}$, a limpid, mobile oil, with mustard-oil odour, b. p. 93—94°/11 mm., and a *dimeride* of this, a viscous, odourless oil, b. p. 195—200°/16 mm. The mechanism of the reaction is the same as in the action of epichlorohydrin on sodiomalonic esters and such compounds (Traube and Lehmann, A., 1899, i, 417; 1901, i, 501). The potassiopyrrole is first attached to the oxide ring and then potassium chloride is eliminated; thus,

$$C_4H_4NK + \underset{\diagdown O \diagup}{CH_2-CH}\cdot CH_2Cl = C_4H_4N\cdot CH_2\cdot CH(OK)\cdot CH_2Cl \longrightarrow$$

$$C_4H_4N\cdot CH_2\cdot \underset{\diagdown O \diagup}{CH-CH_2} + KCl.$$

This course would account for the production of the dimeride, and is supported by the fact that monochlorohydrin and potassiopyrrole yield propylene oxide, pyrrole, and potassium chloride.

Dichloro*iso*propyl acetate (acetyldichlorohydrin) also reacted with potassiopyrrole to form the above oxide and its dimeride. In this case the hydrin seems to decompose into epichlorohydrin and acetyl chloride, for the product also contains a new *diacetylpyrrole*, $C_8H_9O_2N$, which remains behind as the potassium salt when the other substances are extracted with ether. The compound forms rectangular prisms, m. p. 55°, b. p. 105°/16 mm.

The above α-1-pyrrylpropylene βγ-oxide was used in a number of reactions. Thus, with an ethereal solution of magnesium ethyl bromide, it reacted without any evolution of ethane to give *γ-bromo-α-1-pyrrylpropan-β-ol*, $C_4H_4N\cdot CH_2\cdot CH(OH)\cdot CH_2Br$, as a colourless syrup, b. p. 137—139°/14 mm., whilst in boiling benzene it gave, in addition, a new *pyrryl alcohol*, probably

$$C_4H_4N\cdot CH_2\cdot CH(OH)\cdot CH_2Et,$$

as a limpid oil with a faint odour, b. p. 115—117°/14 mm. The bromohydrin was converted into the acetate, *γ-bromo-α-1-pyrryl*iso*propyl acetate*, $C_4H_4N\cdot CH_2\cdot CH(OAc)\cdot CH_2Br$, by the action of magnesium ethyl bromide, followed by acetyl chloride, and, by

similar means, into the p-*nitrobenzoate*, $C_{14}H_{13}O_4N_2Br$, m. p. 79—80°. The acetate is an unstable, aromatic syrup which gives a number of products when left with sodium methoxide, of which only the chief has been isolated. This is probably *γ-methoxy-α-*1-*pyrrylpropan-β-ol*, $C_4H_4N{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OMe$, which has b. p. 143°/12 mm.

The propylene oxide readily combines with water when heated at 100° in an atmosphere of nitrogen in a sealed tube, to form *α-*1-*pyrrylpropane-βγ-diol*, as a limpid, viscous oil, b. p. 167—168°/15 mm., with a bitter taste. It also absorbs hydrogen chloride in cold, ethereal solution, yielding *γ-chloro-α-*1-*pyrrylpropan-β-ol*, $C_4H_4N{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl$, b. p. 109—110°/12 mm., 122·5°/19 mm. This was methylated by means of methyl iodide and silver oxide, the reaction requiring special care, and *γ-chloro-β-methoxy-α-*1-*pyrrylpropane*, $C_4H_4N{\cdot}CH_2{\cdot}CH(OMe){\cdot}CH_2Cl$, was obtained as a mobile, fragrant oil, b. p. 103·5—105°/20 mm. Attempts were made to eliminate hydrogen chloride from this, and potassiopyrrole was found to be effective. This gives a mixture of pyrrole, a bicyclic *compound*, probably of the formula

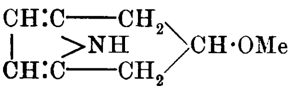
$$CH{<}\begin{matrix}CH{:}C{\cdot}CH_2\\ \quad | \\ CH{\cdot}N{\cdot}CH_2\end{matrix}{>}CH{\cdot}OMe,$$

a mobile oil with an intense, not unpleasant odour, b. p. 73—74°/20 mm., and *β-methoxy-αγ-di-*1-*pyrrylpropane*,

$$(C_4H_4N{\cdot}CH_2)_2CH{\cdot}OMe,$$

a very stable, viscous oil, b. p. 149·5—150·5°/20 mm. Methyl-alcoholic potassium hydroxide also effects the removal of hydrogen chloride, giving the above bicyclic compound and also *β-methoxy-α-*1-*pyrrylpropan-γ-ol*, $C_4H_4N{\cdot}CH_2{\cdot}CH(OMe){\cdot}CH_2{\cdot}OH$, b. p. 105—108°/26 mm.

Dichlorohydrin was also methylated by carefully treating a solution of it in methyl iodide with silver oxide. The *dichloro*iso*propyl methyl ether*, $CH(CH_2Cl)_2{\cdot}OMe$, thus obtained, is a mobile, highly refractive, very volatile oil with a refreshing odour, b. p. 47·5°/20 mm., 159—159·5°/740 mm., which reacts with potassiopyrrole in benzene solution to give the above bicyclic compound, $C_8H_{11}ON$, and an *isomeride*, probably of the formula (annexed), which is an unstable oil, b. p. 104·5—106°/11 mm.



s-Dichloroacetone was boiled with acetic acid and excess of anhydrous potassium acetate, and thus converted into *chloroacetylmethyl acetate*, $CH_2Cl{\cdot}CO{\cdot}CH_2{\cdot}OAc$, b. p. 112—114°/16 mm. J. C. W.

3-*gem*-Dimethylpiperidine. JOHN GUNNING MOORE DUNLOP (the late) (T., 1915, **107**, 1712—1713).—*αα*-Dimethylglutarimide has been reduced by means of sodium and boiling amyl alcohol to 3:3-*dimethylpiperidine*, a strongly alkaline base with b. p. 137°, which forms a deliquescent *hydrochloride*, a *hydriodide*, m. p. 200°, an *aurichloride*, needles, m. p. 182°, and a *benzoyl* derivative, needles, m. p. 68—69°, b. p. 204°/15 mm. It was desired to convert the base into 3:3-dimethyl-1:1-trimethylenepiperidinium

iodide, in connexion with another research (compare T., 1912, **101**, 1748), but this could not be realised. J. C. W.

Preparation of a Carbonate of Sodium 2-Phenylquinoline-4-carboxylate. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P., 285499; from *J. Soc. Chem. Ind.*, 1915, **34**, 1167).—A *compound*, $C_{16}H_{10}O_2NNa + C_{16}H_{11}O_2N + H_2CO_3$, which has more therapeutic value than 2-phenylquinoline-4-carboxylic acid or its sodium salt, is obtained by the interaction of this acid and sodium carbonate or sodium hydrogen carbonate, of the sodium salt and carbon dioxide, or of 2-phenylquinoline-4-carboxylates and sodium hydrogen carbonate. J. C. W.

Derivatives of *o*-Aminophenol and α-Amino-β-naphthol. E. VON MEYER (*J. pr. Chem.*, 1915, [ii], **92**, 255—271).—An investigation of the benzoxazolone compounds obtainable from *o*-aminophenols and α-amino-β-naphthol by the action of carbonyl chloride.

[With HUGO SAHLAND.]—1 : 2-Dihydrobenzoxazolone (carbonyl-*o*-aminophenol), $C_6H_4<{NH \atop -O-}>CO$, can be produced in better yield than that previously obtained (Schmitt and Hentschel, *ibid.*, 1888, [ii], **37**, 27) by allowing the action of the carbonyl chloride and *o*-aminophenol to occur in pyridine solution. With care, *o-hydroxyphenylcarbamic acid*, $OH\cdot C_6H_4\cdot NH\cdot CO_2H$, m. p. 95°, can be isolated as an intermediate product, which at 100° passes into the oxazolone compound; the *silver* salt undergoes a similar dehydration at 110°. By treatment with phenylcarbimide and in alkaline solution with ethyl chloroformate, dihydrobenzoxazolone is respectively converted into *ethyl* 1 : 2-*dihydrobenzoxazolone*-2-*carboxylate*, $O<{C_6H_4 \atop -CO-}>N\cdot CO_2Et$, leaflets, m. p. 78°, and the corresponding *anilide*, $O<{C_6H_4 \atop -CO-}>N\cdot CO\cdot NHPh$, short needles, m. p. 125°; a *benzoyl* derivative, $O<{C_6H_4 \atop -CO-}>NBz$, crystals, m. p. 165°, and a *nitro*-derivative, $CO<{NH \atop -O-}>C_6H_3\cdot NO_2$, yellow needles, m. p. 242°, were also prepared. Interaction with aniline produced a substance, probably the *anil*, $C_6H_4<{NH \atop -O-}>C:NPh$, insoluble in alkalis.

Under similar conditions to the preceding, α-amino-β-naphthol was converted into 1 : 2-*dihydronaphthoxazolone* (*carbonylaminonaphthol*), $C_{10}H_6<{NH \atop -O-}>CO$, prisms, m. p. 206°, which, when heated with concentrated hydrochloric acid at 150°, undergoes fission into the original aminonaphthol and carbon dioxide. Treatment in alcoholic solution with methyl and ethyl iodide in the presence of potassium hydroxide produced respectively 2-*methyl*-1 : 2-*dihydronaphthoxazolone*, $C_{10}H_6<{NMe \atop -O-}>CO$, very pale red needles, m. p. 184°, and its 2-*ethyl*-analogue, $C_{10}H_6<{NEt \atop -O-}>CO$, needles, m. p.

141°. Acetylation and benzoylation yielded respectively 2-*acetyl*-1 : 2-*dihydronaphthoxazolone*, $C_{10}H_6<\substack{NAc \\ -O-}>CO$, pale red needles, m. p. 121°, and the corresponding 2-*benzoyl* compound, colourless needles, m. p. 256°. Treatment with aniline at 250° effected fission of the heterocyclic ring with formation of *β-hydroxy-α-naphthyl-aminoformanilide*, $OH \cdot C_{10}H_6 \cdot NH \cdot CO \cdot NHPh$, needles, m. p. 229° In cold acetic acid solution, chlorine converted the naphthoxazolone compound into *α-chloro*-1 : 2-*dihydronaphthoxazolone*,

$$C_{10}H_5Cl<\substack{NH \\ -O-}>CO,$$

unfused at 310°, whereas in chloroform solution the product was an isomeric *β-chloro*-compound, pale yellow crystals of high m. p.; longer treatment with chlorine in hot acetic acid solution gave rise to dichloro-β-naphthaquinone. By heating with phosphorus pentachloride and treating a hot acetic acid solution with chlorine, a very pale red *dichloro*-1 : 2-*dihydronaphthoxazolone*,

$$C_{10}H_4Cl_2<\substack{NH \\ -O-}>CO,$$

of high m. p., and a *tetrachloroacetyl*-1 : 2-*dihydronaphthoxazolone*, a yellow, crystalline solid, m. p. 75°, possibly of the structure $O<\substack{C_{10}H_5Cl \\ -CO-}>N \cdot CO \cdot CCl_3$, were respectively obtained. Similarly, by bromination in acetic acid solution, a *bromo*-1 : 2-*dihydronaphthoxazolone*, $C_{10}H_5Br<\substack{NH \\ -O-}>CO$, yellow needles, decomp. at 250°, and a *dibromo*-derivative, $C_{10}H_4Br_2<\substack{NH \\ -O-}>CO$, yellow needles, m. p. above 300°, were obtained. Nitration in acetic acid solution by nitric acid or nitrous fumes, in the latter case using a hot solution, yielded a *nitro*-1 : 2-*dihydronaphthoxazolone*, $NO_2 \cdot C_{10}H_5<\substack{NH \\ -O-}>CO$, needles, decomp. near 270°, m. p. above 300°, whereas the action of sodium nitrite on a cold acetic acid solution gave 2-*nitroso*-1 : 2-*dihydronaphthoxazolone*, $O<\substack{C_{10}H_6 \\ -CO-}>N \cdot NO$, a yellowish-brown solid decomp. at 170°, m. p. 194°.

[With Paul Rassfeld.]—Methyl 4-amino-3-hydroxybenzoate, ("α-orthoform") is converted by formic acid into a *formyl* derivative, $CHO \cdot NH \cdot C_6H_3(OH) \cdot CO_2Me$, colourless, tetragonal leaflets, m. p. 225°, which at 240° loses water with formation of *methyl benzoxazole*-5-*carboxylate*, $CO_2Me \cdot C_6H_3<\substack{N \\ O}>CH$, yellow needles, m. p. 99°. In a similar manner, the isomeric methyl 3-amino-4-hydroxybenzoate ("β-orthoform") is convertible successively into its *formyl* derivative, silky needles, m. p. 222°, and *methyl benzoxazole*-4-*carboxylate*, small needles, m. p. 107°. The two methyl aminohydroxybenzoates can also be converted into their *acetyl* derivatives, $NHAc \cdot C_6H_3(OH) \cdot CO_2Me$, needles, m. p. 188°, and m. p. 204° respectively, which can be dehydrated by zinc chloride at 100° and by acetic anhydride at 140—150° respectively, giving

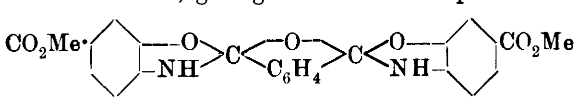
methyl 1-*methylbenzoxazole*-5-*carboxylate*, $CO_2Me\cdot C_6H_3<^{N}_{O}>CMe$, slender needles, m. p. 103—104°, and the isomeric *methyl* 1-*methylbenzoxazole*-4-*carboxylate*, silky needles, m. p. 66°.

Methyl 4-amino-3-hydroxybenzoate forms, with ethyl oxalate, an *additive* compound, $C_{22}H_{28}O_{10}N_2$, needles, m. p. 112°, which, when heated with excess of the ethyl oxalate, is converted into *methyl oxalyldi*-(4-*amino*-3-*hydroxybenzoate*),

$$C_2O_2[NH\cdot C_6H_3(OH)\cdot CO_2Me]_2,$$

rods, m. p. 298—300°; *ammonium* salt, yellow powder; *diacetyl* derivative, stellar groups of needles, m. p. 171°; *dibenzoyl* derivative, needles, m. p. 231°. Methyl 3-amino-4-hydroxybenzoate gave no additive compound with ethyl oxalate, but on heating a mixture of the two substances, *methyl oxalyldi*-(3-*amino*-4-*hydroxybenzoate*), needles, m. p. 312—313°, was obtained, which was also produced from a solution of the oxalate of the amino-ester on prolonged boiling.

When fused with phthalic anhydride, methyl 4-amino-3-hydroxybenzoate reacts, giving a condensation product of the possible constitution (annexed formula), prisms, m. p. 229° The same



ester in dilute sodium hydroxide solution, when treated with a toluene solution of carbonyl chloride, gave leaflets, m. p. 228°, of *methyl* 1:2-*dihydrobenzoxazolone*-5-*carboxylate*,

$$CO_2Me\cdot C_6H_3<^{NH}_{O}>CO,$$

the alternative enolic constitution, $CO_2Me\cdot C_6H_3<^{N}_{O}>C\cdot OH$, also being possible; the compound gives a *methyl* derivative, needles, m. p. 168°, and an *acetyl* derivative, leaflets, m. p. 170°.

The interaction of methyl 3-amino-4-hydroxybenzoate and carbonyl chloride has already been investigated (Einhorn and Ruppert, A., 1903, i, 257). The action of carbon disulphide on this ester in alcoholic solution at 160—170° gives *methyl thio*-1:2-*dihydrobenzoxazole*-4-*carboxylate*, $CO_2Me\cdot C_6H_3<^{NH}_{O}>CS$, needles, m. p. 228°, which, from its ability to dissolve in alkalis, may have the tautomeric constitution, $CO_2Me\cdot C_6H_3<^{N}_{O}>C\cdot SH$. With the isomeric 4-amino-3-hydroxy-ester, interaction with carbon disulphide occurs less smoothly.

With nitrous acid, methyl 4-amino-3-hydroxybenzoate and its 3-amino-4-hydroxy-isomeride are converted into *diazoanhydrides*, $CO_2Me\cdot C_6H_3<^{N}_{O}>N$, yellow solids decomp, at 70° and 117° respectively, with feeble explosion. Both products couple with phenols, giving dyes. D. F. T.

Preparation of Ether-like Derivatives of Barbituric Acid. CHEMISCHE WERKE VORM. H. BYK (D.R.-P., 285636; from *J. Soc. Chem. Ind.*, 1915, **34**, 1167).—Alkylalkyloxyalkyl- or dialkyloxyalkylmalonic acids or their derivatives are condensed with carbamide in the usual way, giving products which are less toxic than diethylbarbituric acid. Examples: Ethyl malonate, sodium ethoxide, β-iododiethyl ether, and carbamide yield *di-β-ethoxyethylmalonylcarbamide*, and ethyl malonate, sodium ethoxide, β-iododiethyl ether, ethyl iodide, and carbamide yield *ethyl-β-ethoxyethylmalonylcarbamide*, and in turn from these 5:5-*di(β-ethoxyethyl)barbituric acid* and 5-*ethyl*-5-*β-ethoxyethylbarbituric acid* are formed. J. C. W.

The Condensation of Aldehyde Diacetates and of Phenylhydrazones with 2-Thiohydantoin. BEN H. NICOLET (*J. Amer. Chem. Soc.*, 1915, **37**, 2753—2756).—It is already known that aromatic aldehydes can be condensed with hydantoin, 2-thiohydantoin, and substituted derivatives of the latter, by boiling together with acetic acid and sodium acetate (Wheeler and Hoffmann, A., 1911, i, 498; Wheeler and Brautlecht, A., 1911, i, 500; Wheeler, Nicolet, and Johnson, A., 1911, i, 1031). The value of the condensation lies in the possibility of reducing the products to benzylhydantoins, which are readily hydrolysed to phenylalanines. The author now shows that the aldehyde in this condensation may be replaced by its diacetate or phenylhydrazone; the use of the latter derivative especially enables condensation products to be formed in cases where the corresponding aldehyde would be too volatile.

Under the usual conditions of the condensation, benzylidene diacetate and 2-thiohydantoin gave rise to 2-thio-4-benzylidenehydantoin, and benzaldehydephenylhydrazone yielded the same product. With acetaldehydephenylhydrazone and 2-thiohydantoin the product was 2-*thio*-4-*ethylidenehydantoin*, $\begin{matrix} NH\cdot CO \\ | \\ CS\cdot NH \end{matrix}\!\!>C{:}CHMe$, a yellowish-brown, crystalline powder, m. p. rather indefinite at 253°. D. F. T.

2:4:6-Triaminopyridine. HANS MEYER and ERICH RITTER VON BECK (*Monatsh.*, 1915, **36**, 731—749. Compare Meyer and others, A., 1912, i, 514; 1913, i, 530; 1914, i, 438, 439).—In an attempt to obtain 2:4:6-triaminopyridine, citrazinic acid (2:6-dihydroxypyridine-4-carboxylic acid) was converted by the action of phosphoryl chloride at 200° into 2:6-dichloropyridine-4-carboxylic acid, of which the *methyl ester*, $C_5H_2NCl_2\cdot CO_2Me$, needles, m. p. 82°, on treatment with hydrazine hydrate at water-bath temperature, readily gave 2-*chloro*-6-*hydrazinopyridine*-4-*carboxylhydrazide*, $NH_2\cdot NH\cdot C_5H_2NCl\cdot CO\cdot NH\cdot NH_2$, needles, m. p. 226°, with reddening, but the product obtained by working in alcoholic solution was 2:6-*dichloropyridine*-4-*carboxylhydrazide*, $C_5H_2NCl_2\cdot CO\cdot NH\cdot NH_2$, needles, m. p. 184°. This substance, when treated in very dilute hydrochloric acid solution with sodium nitrite, gave 2:6-*dichloro*-

pyridine-4-carboxylazide, $C_5H_2NCl_2 \cdot CO \cdot N_3$, a pungent, feebly explosive powder, m. p. 89°, which yielded *ethyl* 2 : 6-*dichloro*-4-*pyridylcarbamate*, $C_5H_2NCl_2 \cdot NH \cdot CO_2Et$, needles, m. p. 132°, when boiled with alcohol; hydrolysis of this substance with aqueous alcoholic potassium hydroxide solution caused almost quantitative formation of 2 : 6-*dichloro*-4-*aminopyridine*, $C_5H_2NCl_2 \cdot NH_2$, colourless needles, m. p. 176°.

2 : 6-Dichloropyridine-4-carboxylic acid was also heated at 210° with a concentrated solution of ammonia and a little copper bronze, when 2 : 6-*diaminopyridine*-4-*carboxylic acid*, $C_5H_2N(NH_2)_2 \cdot CO_2H$, was obtained as a sparingly soluble powder, the *methyl* ester, very pale yellow needles, m. p. 173° (*dihydrochloride*, greenish-yellow needles, m. p. 208°, with decomp.; *dibenzoyl* derivative, needles, m. p. 312°), of which slowly reacted with concentrated ammonia solution at the ordinary temperature, giving 2 : 6-*diaminopyridine*-4-*carboxylamide*, $C_5H_2N(NH_2)_2 \cdot CO \cdot NH_2$, leaflets, m. p. 256° (decomp.). The methyl ester of the diaminopyridinecarboxylic acid failed to react with hydrazine hydrate in boiling alcoholic solution, but in the absence of the alcohol the two substances interacted readily, giving the *hydrazide*, $C_5H_2N(NH_2)_2 \cdot CO \cdot NH \cdot NH_2$, colourless needles, m. p. 260° (decomp.), in an open tube. It was not found possible to convert the hydrazide into the corresponding azoimide derivative, probably on account of nitrous acid simultaneously affecting the amino-groups, and endeavours to apply the corresponding dibenzoyldiamino-derivative to the reaction with nitrous acid were foiled by the failure to obtain this substance from the action of methyl dibenzoyldiaminopyridinecarboxylate on hydrazine hydrate, the product being the diaminopyridinecarboxylhydrazide itself. In the absence of copper bronze the reaction product obtained from 2 : 6-dichloropyridine-4-carboxylic acid and concentrated ammonia solution at 200° was 2-*chloro*-6-*aminopyridine*-4-*carboxylic acid*, needles of high m. p. (decomp.).

The aim of the investigation was successfully achieved by heating 2 : 6-dichloro-4-aminopyridine with *p*-toluenesulphonamide, together with sodium carbonate and a little copper bronze, at 180—190°, and hydrolysing the resulting 4-*amino*-2 : 6-*di*-p-*toluenesulphonyldiaminopyridine*, $NH_2 \cdot C_5H_2N(NH \cdot SO_2 \cdot C_6H_4Me)_2$, lustrous needles, decomp. above 360°, with concentrated sulphuric acid, when 2 : 4 : 6-*triaminopyridine*, $C_5H_2N(NH_2)_3$, was obtained as colourless needles, m. p. 185°; the *platinichloride*, reddish-yellow needles, readily decomposes with liberation of platinum. D. F. T.

[Methylphenazonium Iodides.] F. KEHRMANN (*Ber.*, 1915, **48**, 1931—1933).—The view that the green methylphenazonium periodide is a half-quinonoid compound is confirmed by its formation from the half-quinonoid iodide by the addition of iodine in alcoholic solution, thus: $C_{13}H_{11}N_2I,C_{13}H_{13}N_2I + I_2 + EtOH = C_{26}H_{24}N_4I_4,EtOH$ (compare A., 1914, i, 331). J. C. W.

Oxidation of Uric Acid in Alkaline Solution. III. ROBERT BEHREND and RUDOLF ZIEGER (*Annalen*, 1915, **410**, 337—373. Compare Behrend, A., 1904, i, 950; Behrend and Schultz, A.,

1909, i, 272).—In tracing the course of the oxidation of uric acid in alkaline solution, Behrend (*loc. cit.*) assumes the intermediate formation of a substance, $CO<\begin{matrix}NH\cdot C(OH)\cdot CO-NH\\ \quad | \qquad\qquad\quad |\\ NH\cdot C(OH)\cdot NH\cdot CO\end{matrix}$. This must be incorrect, because Biltz's uric acid glycol (A., 1912, i, 589), with which the preceding substance should be identical, does not yield allantoin and uroxanic acid by hydrolysis, but is converted into ammonia and syrupy products even by alkali carbonates in the cold.

The suggestion is now made that in its oxidation in alkaline solution, uric acid is ruptured in the 1:6 position, and an intermediate substance, $CO<\begin{matrix}NH\cdot C(OH)\cdot CO_2H\\ | \\ NH\cdot C(OH)\cdot NH\cdot CO\cdot NH_2\end{matrix}$, is produced. Attempts to synthesise this substance from alloxanic acid and carbamide were unsuccessful.

When an aqueous solution of alloxan tetrahydrate and a large excess of carbamide are heated to incipient boiling with 36% hydrochloric acid, *carbamide alloxanate*, $C_4H_4O_5N_2,CO(NH_2)_2$, is obtained, together with a little alloxantin. The former crystallises from water in four-sided, almost rectangular prisms, decomp. 155—156°, and is converted into carbamide nitrate by concentrated nitric acid, and into normal or acid calcium alloxanate by calcium salts. Carbamide alloxanate can also be obtained by warming uric acid glycol with 35% hydrochloric acid at not more than 50°.

When alloxan tetrahydrate is dissolved in warm water, and the cooled solution, after removal of any alloxantin by filtration, is treated with carbamide, a *substance*, $C_5H_8O_6N_4$, colourless crystals, decomp. 117° or 133—134°, is obtained which appears to be a salt-like compound of carbamide and alloxan monohydrate. It yields carbamide nitrate by treatment with nitric acid, and is converted by heating, alone or with glacial acetic acid, into uric acid glycol; when boiled with acetic anhydride it yields an anhydride, $C_5H_6O_5N_4$, microscopic needles, decomp. 185—186°.

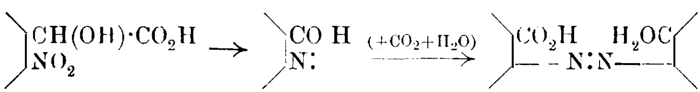
Potassium alloxan, $C_4H_3O_5N_2K$, pale red needles, decomp. about 235°, is obtained by dissolving alloxan tetrahydrate in warm water and treating the cooled, filtered solution with 50% potassium hydroxide at 0°. Methods are described for utilising this salt for the preparation of potassium alloxanate, carbamide alloxanate, and alloxanic acid. *Methyl alloxanate*, $C_5H_6O_5N_2$, prisms, decomp. 175—176°, can only be obtained by warming alloxanic acid with thionyl chloride at 40—50° and heating the resulting, solid chloride with methyl alcohol. The aqueous solution of the ester reacts strongly acid towards litmus and decomposes hydrogen carbonates, but is easily hydrolysed by 10% potassium hydroxide. C. S.

Constitution and Colour. IV. Colour of Azo-compounds and their Salts. F. KEHRMANN (*Ber.*, 1915, **48**, 1933—1938. Compare A., 1908, i, 699, 993; 1913, i, 1320).—Since azo-compounds contain two nitrogen atoms, each of which may become the point of attachment of an acid by exerting its two additional valencies,

they should give rise to two series of salts. This point has been tested by dissolving some azo-compounds in sulphuric acid of various strengths.

Azobenzene gives a very deep golden-yellow solution in concentrated sulphuric acid, but a deep red in acid containing 25% SO_3, which, however, soon becomes paler owing to sulphonation. *p*-Aminoazobenzene gives a red solution in acid containing 25% SO_3, a golden-yellow in the ordinary concentrated acid, and a bluish-red in an acid of a certain dilution. Chrysoidin gives a golden-yellow solution in the concentrated acids and a bluish-red in diluted acid. In the case of azobenzene, it is suggested that the two colours are due to the mono-acid and the di-acid salts. The other cases are explained on the assumption that salt formation at the chromophore causes a deepening of colour, whereas at the amino-group it usually causes a lessening. J. C. W.

A Decomposition of Certain *o*-Nitromandelic Acids. GERTRUDE MAUD ROBINSON and ROBERT ROBINSON (T., 1915, **107**, 1753—1762).—In a previous communication (T., 1914, **105**, 1466) it was noted that 6-nitro-3:4-methylenedioxymandelic acid gave rise to a dark brown product when boiled with nitrobenzene. The nature of the decomposition has now been revealed, in the first instance by a study of the action of heat on 6-nitro-3:4-dimethoxymandelic acid, and it is found that the chief products are azobenzenedicarboxylic acids. The oxygen of the nitro-group oxidises the hydroxy-acid chain, and the complete reaction may be represented thus:



6-*Nitro*-3:4-*dimethoxymandelic acid*,

$$NO_2\cdot C_6H_2(OMe)_2\cdot CH(OH)\cdot CO_2H,$$

was prepared by the hydrogen cyanide synthesis from 6-nitroveratraldehyde, in pale yellow needles, m. p. 169—172° (decomp.). When this was heated in nitrobenzene, a vigorous action took place, and 4:5:4′:5′-*tetramethoxyazobenzene*-2:2′-*dicarboxylic acid*,

$$[CO_2H\cdot C_6H_2(OMe)_2]_2N_2,$$

was deposited in crystals resembling hæmatite in colour and lustre. On triturating this with nitric acid (D 1·45) it yielded 2:2′-*dinitro*-4:5:4′:5′-*tetramethoxyazobenzene*, $[NO_2\cdot C_6H_2(OMe)_2]_2N_2$, which crystallised from nitrobenzene in brilliant red needles, m. p. 315° (decomp.). An orange-coloured *modification* of the same compound, identical in m. p., was obtained by the nitration of azoveratrole by cold nitric acid (D 1·42) in acetic acid. Both forms dissolved in sulphuric acid with intense blue colours, but they were recovered in their original forms on dilution, which precludes the idea of *cis-trans*-isomerism. Both forms were also reduced by stannous chloride to 4:5-diaminoveratrole, which was isolated as 2:3-dimethoxyphenanthraphenazine, m. p. 259—261°, by treatment with phenanthraquinone (compare Moureu, 1896).

Azoveratrole was obtained by a modification of Kauffmann and Kugel's method (A., 1911, i, 930) in glistening orange prisms, m. p. 182°, and not 163°. When this was suspended in acetic acid and treated with fuming nitric acid, it yielded, apparently, N : 2 : 2′-*trinitro*-4 : 5 : 4′ : 5′-*tetramethoxyhydrazobenzene*,

$$NO_2 \cdot C_6H_2(OMe)_2 \cdot NH \cdot N(NO_2) \cdot C_6H_2(OMe)_2 \cdot NO_2,$$

yellow needles, m. p. 228°, which was also converted into 2 : 3-dimethoxyphenanthraphenazine, as above.

The decomposition of 6-nitro-3 : 4-methylenedioxymandelic acid, by heating in nitrobenzene solution, differed somewhat from the above reaction in that nitrogen was also evolved. The chocolate-coloured product contained about 25% of other products besides the 4 : 5 : 4′ : 5′-*dimethylenetetraoxyazobenzene*-2 : 2′-*dicarboxylic acid*, $[CH{:}O_2{:}C_6H_2(CO_2H)]_2N_2$, but only this could be isolated. This was achieved through the *sodium* salt, yellow leaflets, and the acid was obtained in opaque masses of brick-red crystals, m. p. 270° (decomp.). On nitration, the carboxyl groups were replaced by nitroxyl, giving 2 : 2′-*dinitro*-4 : 5 : 4′ : 5′-*dimethylenetetraoxyazobenzene*, $C_{14}H_8O_8N_4$, in crimson needles, m. p. 305° (decomp.), which was reduced and then condensed with phenanthraquinone, as above, with the formation of 2 : 3-*methylenedioxyphenanthraphenazine*, $CH_2{:}O_2{:}C_6H_2{<}\begin{matrix} N{:}C \cdot C_6H_4 \\ N{:}C \cdot C_6H_4 \end{matrix}$, pale yellow needles, m. p. 305°.

6-*Nitrohomopiperonyl chloride*, $CH_2{:}O_2{:}C_6H_2(NO_2) \cdot CH_2Cl$, was obtained by saturating an acetic acid solution of homopiperonyl alcohol with hydrogen chloride and then gradually adding nitric acid. It formed pale pink leaflets, m. p. 86°, and irritated the skin. When heated with nitrobenzene, it changed into the above 4 : 5 : 4′ : 5′-dimethylenetetraoxyazobenzene-2 : 2′-dicarboxylic acid, whilst cold methyl-alcoholic potassium hydroxide converted it into 2 : 2′-*dinitro*-4 : 5 : 4′ : 5′-*dimethylenetetraoxystilbene*,

$$[CH_2{:}O_2{:}C_6H_2(NO_2)]_2C_2H_2,$$

brownish-red needles, not molten at 350°.

The above azobenzene derivatives are characterised by giving intense blue solutions in concentrated sulphuric acid, even with the merest traces. J. C. W.

The Preparation of Aliphatic Aminohydrazines. AUGUST DARAPSKY and HANS SPANNAGEL (*J. pr. Chem.*, 1915, [ii], **92**, 272—296).—A record of the results of a series of unsuccessful endeavours to prepare aliphatic aminohydrazines of the type $NH_2 \cdot CR \cdot CR' \cdot NH \cdot NH_2$.

The product of the interaction of diacetylmonoxime and hydrazine varies with the solvent. In aqueous solution a mixture of the former with hydrazine sulphate yielded the ketazine

$$OH \cdot N{:}CMe \cdot CMe{:}N \cdot N{:}CMe \cdot CMe{:}N \cdot OH$$

(compare Forster and Day, T., 1912, **101**, 2240); *dibenzoyl* derivative, orange-red scales, m. p. 215°. In alcoholic solution, using hydrazine hydrate, the product is diacetylhydrazoxime,

$$OH \cdot N{:}CMe \cdot CMe{:}N \cdot NH_2,$$

m. p. 138°, which has also been recently described (*loc. cit.*). This

is unstable in aqueous solution, readily undergoing conversion into the ketazine and hydrazine, but is more stable in alcoholic solution, and in this solvent reacts with aromatic aldehydes, giving normal condensation products; thus, with salicylaldehyde, *o-hydroxybenzylidenediacetylhydrazoxime*, $OH\cdot N{:}CMe\cdot CMe{:}N\cdot N{:}CH\cdot C_6H_4\cdot OH$, yellow needles, m. p. 168°, was obtained. An attempt to confirm the structure of this substance by an independent formation from diacetylmonoxime and *o*-hydroxybenzylidenehydrazine, failed on account of the refusal of these compounds to interact. Diacetylhydrazoxime gave a *benzoyl* derivative, yellow needles, m. p. 201°, and reacted with phenylthiocarbimide, giving a *thiosemicarbazone*, $OH\cdot N{:}CMe\cdot CMe{:}N\cdot NH\cdot CS\cdot NHPh$, flesh-red needles, m. p. 201°. If a mixture of diacetylmonoxime and hydrazine hydrate, in the absence of a solvent, is boiled for several hours, the oximino-group is replaced by the hydrazone group with the formation of diacetyldihydrazone, $NH_2\cdot N{:}CMe\cdot CMe{:}N\cdot NH_2$, m. p. 157° (*dibenzylidene* derivative, yellow needles, m. p. 120°; *di-o-hydroxybenzylidene* derivative, yellow needles, m. p. 245°), which in alcoholic solution, in the presence of dilute hydrochloric acid, undergoes change into dimethylaziethane, $CMe\lessdot\genfrac{}{}{0pt}{}{N\text{---}}{CMe}\gtrdot N$, (compare Curtius and Thun, A., 1891, 1356).

On account of the instability of diacetylhydrazoxime, reduction to the desired aminohydrazine could not be effected, and attention was therefore turned to the reduction of the more stable ketazine, but without achieving the isolation of any reduction product. Benzilhydrazoxime (compare Forster and Day, *loc. cit.*) was then submitted to reduction with sodium amalgam in alcoholic solution, but the product was *meso*-diphenylethylenediamine,

$$NH_2\cdot CHPh\cdot CHPh\cdot NH_2$$

(Japp and Moir, T., 1900, **77**, 644). In an attempt to prepare benzilhydrazoxime by the action of hydroxylamine hydrochloride on benzilhydrazone, a yellow *substance*, m. p. above 280°, not showing the properties of an oxime, was obtained.

Aminoacetophenone hydrochloride, when treated in cold aqueous solution with hydrazine hydrate, yielded diphenyldihydropyrazine, the hydrazine hydrate merely acting as an alkali (compare Gabriel, A., 1908, i, 464), whilst with the heated reagents, in the absence of a solvent, *aminoacetophenoneazine*,

$$NH_2\cdot CH_2\cdot CPh{:}N\cdot N{:}CPh\cdot CH_2\cdot NH_2,$$

colourless needles, m. p. 157°, was obtained. When a solution of aminoacetophenone hydrochloride and hydrazine hydrochloride was neutralised with sodium hydroxide, the effect on the first substance was merely that of an alkali, the product being anhydrobisphenacylamine (compare Gabriel, *loc. cit.*).

β-Bromopropylamine hydrobromide reacted with hydrazine hydrate in aqueous solution, giving a basic, viscous *oil*, the composition of which was represented approximately by the formula C_3H_7N; this gave an oily *benzoyl* derivative. β-Hydroxy-αβ-diphenylethylamine was converted by phosphorus pentachloride into stilbene dichloride, but the desired chlorodiphenylethylamine,

$NH_2 \cdot CHPh \cdot CHPhCl$, was produced by shaking a suspension of the hydrochloride of the hydroxydiphenylethylamine in acetyl chloride with phosphorus pentachloride, being obtained as an oil; *hydrochloride*, m. p. 233° (decomp.); *platinichloride*, deep yellow needles, m. p. 204°; *nitrate*, tablets, m. p. 185°; *benzoyl* derivative, m. p. 195°. Chlorodiphenylethylamine in alcoholic solution is converted by hydrazine hydrate, or also by potassium hydroxide, into *diphenylethyleneimine*, $\begin{matrix} CHPh \\ | \\ CHPh \end{matrix} > NH$, colourless needles, m. p. 83°, which does not reduce potassium permanganate, and is reconverted, even in ethereal solution, by hydrogen chloride into chlorodiphenylethylamine hydrochloride.

Benzo-ε-chloroamylamide, when heated with excess of anhydrous hydrazine, gave an oily product which, when treated in aqueous solution with benzaldehyde, instead of yielding the expected benzoylbenzylidenehydrazinoamylamine,

$$NHBz \cdot [CH_2]_5 \cdot NH \cdot N\colon CHPh,$$

gave benzoylbenzylidenehydrazine, $NHBz \cdot N\colon CHPh$, the chemical change having involved scission of the benzoyl radicle as benzoylhydrazine with concurrent conversion of the chloroamylamine into piperidine. D. F. T.

Transition Points of the Polymorphic Phthalylhydrazides. Frederick Daniel Chattaway and William James Lambert (T., 1915, **107**, 1773—1781).—Phthalylphenylhydrazide and phthalylphenylmethylhydrazide,

$$C_6H_4 < \begin{matrix} CO \\ CO \end{matrix} > N \cdot NHPh \quad \text{and} \quad C_6H_4 < \begin{matrix} CO \\ CO \end{matrix} > N \cdot NMePh,$$

(T., 1911, **99**, 2256, 2261), are well-marked and readily obtainable examples of enantiomerides. The transition points for the two pairs have therefore been determined. This has been done in the first place by measuring the solubilities, then, in the case of the second pair, by observing the growth of the crystals of one form at the expense of the other in acetone, and finally by a dilatometric method. In the case of phthalylphenylhydrazide, the curves for the solubility in alcohol indicate a transition point at about 10°; in chloroform, a little above 9·4°; in ethyl acetate, 9·2°; and in acetone, 9·8°. The two forms are so much more soluble in the last three solvents, and the transformation takes place so much faster, that the transition points are more easily ascertained. The mean is about 9·5°. In the case of phthalylphenylmethylhydrazide, the solubility determination in alcohol indicates a transition point at about 55° (by extrapolation), the second method gives 55—55·5°, and the dilatometric method, 55—55·2°.

In his theoretical deductions concerning the reversible transformation of polymorphic forms, van't Hoff (1897—1898) showed that the ratio of the solubilities of the two forms must be constant for all solvents which only dissolve so little that the laws of dilute solutions are applicable. This conclusion has now been confirmed

experimentally for the first time by the determination of the solubilities of these pairs of hydrazides. J. C. W.

Aromatic-aliphatic Diazoamino Compounds [Arylazodicyanodiamides]. R. VON WALTHER and W. GRIESHAMMER (*J. pr. Chem.*, 1915, [ii], **92**, 209—255).—It has been discovered that not only does guanidine couple with simple diazonium salts, producing stable compounds (investigation unpublished), but that substances allied to guanidine, namely, dicyanodiamide, cyanamide, and dicyanodiamidine, although less basic, behave analogously towards diazo-compounds.

Dicyanodiamide couples with an aromatic diazoxide in alkaline solution, the solution when acidified depositing the diazoamino-compound. The first yield is poor, but more can be obtained by making the filtrate alkaline and again acidifying; it is suggested that this further formation of the diazoamino-compound may be due to the dicyanodiamide in the alkaline solution existing in part as a disodium salt, which alone is active towards the diazo-compound. The hydrogen atom of the $\cdot N_2\cdot NH\cdot$ group in these diazoamino-compounds is replaceable by metals and also by radicles, but from the fact that hydrolysis of the methyl derivative of *p*-tolueneazodicyanodiamide yields methyltoluidine with a little *p*-cresol, it is evident that, in this case at least, alkylation does not entirely follow a single course.

Benzeneazodicyanodiamide and its analogues are generally not very reactive. On hydrolysis in feebly acidic aqueous or alcoholic solution or suspension, the former compound yields dicyanodiamide and tarry products without aniline, thus indicating a structure, $CN\cdot NH\cdot C(:NH)\cdot NH\cdot N_2Ph$, as opposed to

$$CN\cdot NH\cdot C(:NH)\cdot N_2\cdot NHPh.$$

In strongly acidic solution or suspension the products of hydrolysis are phenylguanylcarbamide and free nitrogen. The identity of the phenylguanylcarbamide was demonstrated by an independent synthesis by the hydrolysis of *s*-cyanophenylguanidine (Wheeler, A., 1903, i, 751). In explanation of the difference in behaviour of benzeneazodicyanodiamide towards hydrolysis in feebly and strongly acidic solutions, it is suggested that in the former case the substance possesses its usual *anti*-configuration, thus,

$$\begin{matrix} & NPh \\ & \| \\ CN\cdot NH\cdot C(:NH)\cdot NH\cdot & N \end{matrix} \longrightarrow CN\cdot NH\cdot C(:NH)\cdot NH_2 + N_2 + C_6H_5\cdot OH$$

whereas the stronger acid causes a conversion, through the hydrochloride, into a *syn*-configuration, $\begin{matrix} CN\cdot NH\cdot C(:NH)\cdot NH\cdot N \\ \| \\ PhN \end{matrix}$, the substance, on hydrolysis, readily eliminates nitrogen yielding phenylguanylcarbamide, $NH_2\cdot CO\cdot NH\cdot C(:NH)\cdot NHPh$. The isolation of an unstable hydrochloride lends support to this idea, but in no case have geometrical stereoisomerides been isolated. As is to be expected, the tendency to the addition of hydrogen chloride is less in the more acidic compounds of this class. In the description of these

compounds, the grouping NH:N·NH_2 is termed triazen, the first and third nitrogen atoms being designated by α and γ (Wolff and Lindenhayn, A., 1904, i, 197).

Benzeneazodicyanodiamide (*α-phenyltriazen-γ-cyanaminoiminomethane*), CN·NH·C(:NH)·NH·N_2Ph, was prepared by mixing cold aqueous solutions of benzenediazonium chloride and dicyanodiamide, and treating the diluted solution successively with solutions of sodium hydroxide and hydrochloric acid; the product crystallises in prisms, decomp., with slight explosion, at 123°. It is decomposed, with mild explosion, on contact with sulphuric acid. Boiling water causes decomposition into dicyanodiamide, together with tarry matter in which a little phenol is present, whilst hydrochloric acid of 15% concentration gives rise to phenylguanylcarbamide. The following salts were prepared: *Sodium*, yellow needles; *ammonium*, prisms; *pyridine*, yellow; *silver*, explosive, yellow powder; *lead*, yellow; *cobalt*, bluish-red; *ferric*, yellow; *ferrous*, brown. By treating the sodium salt with an alcoholic solution of methyl iodide, *γ-phenyl-γ-methyltriazen-α-cyanaminoiminomethane*,

CN·NH·C(:NH)·N_2·NMePh,

yellow needles, decomp. at 167—168°, was obtained, whilst with benzyl chloride and *p*-nitrobenzyl chloride in a similar manner, *γ-phenyl-γ-benzyltriazen-α-cyanaminoiminomethane*,

CN·NH·C(:NH)·N_2·NPh·CH_2Ph,

needles, decomp. at 165—166°, and *γ-phenyl-γ-*p*-nitrobenzyltriazen-α-cyanaminoiminomethane*, CN·NH·C(:NH)·N_2·NPh·CH_2·C_6H_4·NO_2, colourless needles, decomp. at 162°, were respectively obtained.

p-*Tolueneazodicyanodiamide* (*α-*p*-tolyltriazen-γ-cyanaminoiminomethane*), CN·NH·C(:NH)·NH·N_2·C_6H_4Me, obtained by diazotising *p*-toluidine and proceeding as in the previous case, forms yellow rhombs, decomp. at 133°; *sodium* salt, yellow needles; *potassium* salt. The action of methyl sulphate on the free compound in the presence of sodium hydroxide solution caused the formation of *γ-*p*-tolyl-γ-methyltriazen-α-cyanaminoiminomethane*,

CN·NH·C(:NH)·N_2·NMe·C_6H_4Me,

yellow needles, decomp. at 155—158°, which, on hydrolysis with dilute acid, gave methyl-*p*-toluidine, dicyanodiamide, and a little *p*-cresol, the formation of the latter probably being due to the presence of an isomeride. An alcoholic solution of benzyl chloride converted the sodium salt into *γ-*p*-tolyl-γ-benzyltriazen-α-cyanaminoiminomethane*, CN·NH·C(:NH)·N_2·N(CH_2Ph)·C_6H_4Me, colourless needles, decomp. at 163°, whilst *p*-nitrobenzyl chloride, under similar conditions, produced *γ-*p*-tolyl-γ-*p*-nitrobenzyltriazen-α-cyanaminoiminomethane*, CN·NH·C(:NH)·N_2·N(C_6H_4Me)·CH_2·C_6H_4·NO_2, yellow needles, decomp. at 158°. An attempt to effect a rearrangement of *p*-tolueneazodicyanodiamide into the corresponding aminoazo-compound by warming with *p*-toluidine and aniline hydrochloride evidently caused fission of the molecule, the isolated product being aminoazo-*p*-toluene.

o-*Tolueneazodicyanodiamide* (*α-*o*-tolyltriazen-γ-cyanaminoiminomethane*), CN·NH·C(:NH)·NH·N_2·C_6H_4Me, obtained in a similar manner, forms yellow needles, decomp. at 114°; *sodium* salt, yellow

needles. *γ-o-Tolyl-γ-methyltriazen-α-cyanaminoiminomethane*, $CN\cdot NH\cdot C(:NH)\cdot N_2\cdot NMe\cdot C_6H_4Me$, yellow leaflets, decomp. at 152°, and *γ-o-tolyl-γ-benzyltriazen-α-cyanaminoiminomethane*,

$$CN\cdot NH\cdot C(:NH)\cdot N_2\cdot N(C_6H_4Me)\cdot CH_2Ph,$$

pale yellow needles, decomp. at 160°, were obtained similarly to their para-isomerides.

m-*Tolueneazodicyanodiamide* (*α*-m-*tolyltriazen-γ-cyanaminoiminomethane*), yellow needles, decomp. at 115° (*potassium* salt less soluble than the *sodium* salt), prepared in the usual manner, was converted into *γ*-m-*tolyl-γ-methyltriazen-α-cyanaminoiminomethane*, yellow needles, decomp. at 148°, and *γ*-m-*tolyl-γ-benzyltriazen-α-cyanaminoiminomethane*, pale yellow needles and prisms, decomp. at 153°.

p-*Chlorobenzeneazodicyanodiamide* (*α*-p-*chlorophenyltriazen-γ-cyanaminoiminomethane*), $CN\cdot NH\cdot C(:NH)\cdot NH\cdot N_2\cdot C_6H_4Cl$, yellow rhombs, decomp. at 140—160° (*pyridine* salt, yellow), was further converted into *γ*-p-*chlorophenyl-γ-methyltriazen-α-cyanaminoiminomethane*, $CN\cdot NH\cdot C(:NH)\cdot N_2\cdot NMe\cdot C_6H_4Cl$, yellow needles, decomp. at 160°, and into *γ*-p-*chlorophenyl-γ-benzyltriazen-α-cyanaminoiminomethane*, $CN\cdot NH\cdot C(:NH)\cdot N_2\cdot N(C_6H_4Cl)\cdot CH_2Ph$, colourless needles, m. p. 170—175°. As with the benzeneazo-compound, no very definite results were obtainable in reduction experiments with the *p*-chlorobenzeneazo-compound, and very little aminodicyanodiamide was produced, if any; a compound (or compounds) separated from the reduction product gave a *picrate*, m. p. 190°, and a pale yellow *benzylidene* derivative, decomp. at 170°.

p-*Bromobenzeneazodicyanodiamide* (*α*-p-*bromophenyltriazen-γ-cyanaminoiminomethane*), $CN\cdot NH\cdot C(:NH)\cdot NH\cdot N_2\cdot C_6H_4Br$, rhombs, decomp. at 160° (*sodium* salt; *pyridine* salt, yellow), prepared in the general manner, was convertible into *γ*-p-*bromophenyl-γ-methyltriazen-α-cyanaminoiminomethane*,

$$CN\cdot NH\cdot C(:NH)\cdot N_2\cdot NMe\cdot C_6H_4Br,$$

yellow needles, decomp. at 185°, and *γ*-p-*bromophenyl-γ-benzyltriazen-α-cyanaminoiminomethane*,

$$CN\cdot NH\cdot C(:NH)\cdot N_2\cdot N(C_6H_4Br)\cdot CH_2Ph,$$

colourless needles, decomp. at 186°.

o-*Carboxybenzeneazodicyanodiamide* (*α*-o-*carboxyphenyltriazen-γ-cyanaminoiminomethane*), $CN\cdot NH\cdot C(:NH)\cdot NH\cdot N_2\cdot C_6H_4\cdot CO_2H$, prepared from diazotised anthranilic acid in the general manner, is a yellow, crystalline solid, decomp. near 98°, which is decomposed by boiling water into salicylic acid, dicyanodiamide, and nitrogen; *sodium* salt, $C_{18}H_{13}O_4N_{12}Na_3$; *silver* salt, $C_{18}H_{13}O_4N_{12}Ag_3$, an amorphous, yellow solid. Attempts to prepare a methyl or benzyl derivative by way of the sodium salt were unsuccessful.

In an endeavour to convert benzeneazodicyanodiamide and its derivatives into the ethyl ester of the corresponding carboxylic acids by treatment with alcoholic hydrogen chloride, it was discovered that nitrogen was eliminated with formation of an arylguanylcarbamide. There were thus prepared: p-*Chlorophenylguanylcarbamide*, $C_6H_4Cl\cdot NH\cdot C(:NH)\cdot NH\cdot CO\cdot NH_2$, colourless rhombs, m. p. 125°; *hydrochloride*, prisms, m. p. 172—173°; *platini-*

chloride, yellow prisms; *picrate*, m. p. 195°; *silver* salt, colourless; *acetyl* derivative, $C_6H_4Cl·NAc·C(:NH)·NH·CO·NH_2$, prisms, m. p. 150—151°. *Phenylguanylcarbamide*, $NHPh·C(:NH)·NH·CO·NH_2$, colourless, hexagonal prisms, m. p. 62—63°; *hydrochloride*, prisms, m. p. 174—175°; *picrate*, m. p. 181—182°. p-*Tolylguanylcarbamide*, $C_6H_4Me·NH·C(:NH)·NH·CO·NH_2$, rectangular leaflets, m. p. 143°; *hydrochloride*, prisms, m. p. 167—168°. o-*Tolylguanylcarbamide*, octahedra, m. p. 136°; *hydrochloride*, needles, m. p. 73—74°. m-*Tolylguanylcarbamide*, hexagonal leaflets, m. p. 97—98°; *hydrochloride*, prisms, m. p. 183—184°. p-*Bromophenylguanylcarbamide*, $C_6H_4Br·NH·C(:NH)·NH·CO·NH_2$, prisms, m. p. 152°; *hydrochloride*, leaflets, m. p. near 170°. o-*Carboxyphenylguanylcarbamide*, $CO_2H·C_6H_4·NH·C(:NH)·NH·CO·NH_2$, prisms or needles, decomp. at 275—280°; *silver* salt, $C_9H_8O_3N_4Ag_2$. An endeavour to extend the investigation of the effect of alcoholic hydrogen chloride to the methyl derivatives of the above compounds was prevented by the complexity of the reaction with these substances.

In the course of experiments attempting the synthesis of phenylguanylcarbamide by an independent method, *substances*, m. p. 155°, 130°, and above 280°, were obtained from the interaction of silver cyanocarbamide and aniline hydrochloride under varying conditions. The interaction of phenylguanidine nitrate and potassium cyanate under varying conditions yielded *phenylguanidine carbonate*, prisms, m. p. 138° (decomp.), and a sparingly soluble *substance*, m. p. above 290°, but failed to give the desired phenylguanylcarbamide, which was, however, successfully produced by heating cyanophenylguanidine, $CN·NH·C(:NH)·NHPh$, with dilute hydrochloric acid. *Methylthiolphenylbiuret*,

$$SMe·C(:NPh)·NH·CO·NH_2,$$

colourless needles, m. p. 156°, was obtained by a similar hydrolysis of *s*-cyanomethylthiolphenyl*iso*carbamide, $SMe·C(:NPh)·NH·CN$.

The formation of phenylguanylcarbamide from benzeneazodicyanodiamide suggests that cyanophenylguanidine is an intermediate product, and this substance can actually be isolated under suitable conditions. If benzeneazodicyanodiamide in ethereal suspension is treated with hydrogen chloride, an unstable, red substance is obtained which, from its decomposition by warm water into cyanophenylguanidine, hydrogen chloride, and nitrogen, is in all probability the *hydrochloride* of the *syn*-form of benzeneazodicyanodiamide. By a similar procedure, all the benzeneazodicyanodiamide derivatives described above, with the exception of the *o*-carboxy-derivative, which did not form a hydrochloride, were made to yield the corresponding cyano-arylguanidines. There were thus obtained, s-*cyano*-p-*tolylguanidine*, $CN·NH·C(:NH)·NH·C_6H_4Me$, rectangular leaflets, m. p. 207—208°; s-*cyano*-m-*tolylguanidine*, rectangular leaflets, m. p. 193—194°; s-*cyano*-p-*chlorophenylguanidine*,

$$CN·NH·C(:NH)·NH·C_6H_4Cl,$$

rectangular leaflets, m. p. 197—198°; s-*cyano*-p-*bromophenylguanidine*, $CN·NH·C(:NH)·NH·C_6H_4Br$, rectangular leaflets, m. p. 196—197°.

Dicyanodiamidine resembles dicyanodiamide in its ability to

couple with diazo-compounds in alkaline solution, the product obtained with an alkaline diazobenzene solution being *benzeneazodicyanodiamidine* (*a-phenyltriazen-γ-carbamidoiminomethane*), $NH_2\cdot CO\cdot NH\cdot C(:NH)\cdot NH\cdot N_2Ph$, yellow needles, decomp. at 176—177°, which possesses feeble basic and still more feeble acidic properties; *hydrochloride*, yellow prisms, decomp. near 92°; *picrate*, needles, decomp. at 70°. When treated with alcoholic hydrogen chloride solution, this product behaves differently from its dicyanodiamide analogue, giving no cyanophenylcarbamide, but only dicyanodiamidine and tarry matter.

The coupling of cyanoamide in alkaline solution with a benzene diazo-oxide gives benzeneazocyanoamide, which has already been described (Wolff and Lindenhayn, *loc. cit.*). D. F. T.

The Refractive Indices of Solutions of Certain Proteins. IX. Edestin. CARL L. A. SCHMIDT (*J. Biol. Chem.*, 1915, **23**, 487—493).—The solutions of edestin follow the law $n - n_1 = ac$; where n is the observed index of the solution, n_1 of the solvent, c the percentage of protein, and a a constant expressing a change in the refractive index due to the addition of 1% of the protein. In the case of edestin $a = 0.00174 \pm 0.00006$. This remains constant even although the solvent produces hydrolysis. W. D. H.

The Nature of Enzyme Action. IV. The Action of Insoluble Enzymes. W. M. BAYLISS (*J. Physiol.*, 1915, **50**, 85—94).—Urease, lipase, emulsin, invertase, lactase, papain, peroxydase, and catalase are active in media from which they can be filtered off by ordinary paper, whilst the filtrates are inactive. Pepsin and trypsin are much more active in suspensions than are the filtrates; these enzymes are capable of a small degree of colloidal solution in such solutions. Enzymic activity is thus manifested at the interface of contact between the solid enzyme phase and the liquid substrate phase. The catalysts concerned are not in true solution. W. D. H.

The Effect of Sodium Chloride on the Action of Invertase. H. A. FALES and J. M. NELSON (*J. Amer. Chem. Soc.*, 1915, **37**, 2769—2786).—The concentration of hydrogen ion remains constant during the inversion of sucrose by invertase. The addition of sodium in the action may exert a twofold effect: it causes an increase in the concentration of the hydrogen ion if the concentration of the hydrochloric acid present is greater than 0·0001 molar; and also effects a decrease in the activity of the invertase if comparison is made between solutions of the same concentration with regard to hydrogen ion. The latter effect varies according to the concentration of the hydrogen ion and of the sodium chloride, being least at the optimum of the invertase action. The adjustment of the concentration of the hydrogen ion by the addition of mixtures of acids and salts ("buffers"), as sometimes practised, may introduce appreciable error, unless it is restricted to the neighbourhood of the optimum zone where the salt effect is a minimum.

The addition of sodium chloride to solutions of hydrochloric acid

causes an increase in the concentration of the hydrogen ion as measured by the E.M.F. method and by the hydrolysis of sucrose solutions. In the region of enzyme activity it is therefore necessary to measure the concentration of the hydrogen ion, and it is not permissible to calculate it from the concentration of the acid used. D. F. T.

The Retention of Activity by Urease and by Oxydase after Exposure to the Temperature of Liquid Air. JOSEPH SAMUEL HEPBURN and CHARLES BLIZARD BAZZONI (*J. Franklin Inst.*, 1915, **180**, 603—605).—After exposure to the temperature of liquid air for 100 hours, a solution of urease was found to have suffered but slight loss in its power of hydrolysing carbamide. The observed activity was 96·3% of that of the fresh solution. During the same period the activity of a solution, which was kept at 20° in presence of 0·2% of tricresol, was found to have fallen to 44·4%.

Qualitative experiments show also that oxydase retains its power of reacting with Witte's peptone after subjection to the temperature of liquid air for 3½ hours. H. M. D.

Preparation of 2-Chloro-4-dimethylaminobenzene-1-arsinic Acid. C. F. BOEHRINGER & SÖHNE (D.R.-P., 286546; from *J. Soc. Chem. Ind.*, 1915, **34**, 1165).—*m*-Chlorodimethylaniline is treated with arsenic trichloride, and the 2-chloro-4-dimethylaminobenzene-1-arsenoxide so obtained is oxidised by means of hydrogen peroxide, mercuric oxide, or potassium permanganate. Compared with the non-halogenated compound, 2-chloro-4-dimethylaminobenzene-1-arsinic acid is less toxic, but has a greater therapeutic activity. J. C. W.

Preparation of 4 : 4′-Dihydroxy-3 : 3′-diaminoarsenobenzene. LES ÉTABLISSEMENTS POULENC FRÈRES (Eng. Pat., 1914, 21421; from *J. Soc. Chem. Ind.*, 1915, **34**, 1225).—3-Nitro-4-hydroxyphenyl-1-arsinic acid is reduced by zinc and acetic acid at 25—35°, and then in hydrochloric acid solution at 50—60°, in presence of a small quantity of sulphurous acid, and is thereby converted into 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene. The sulphurous acid appears to prevent the reduction being carried past the formation of the arseno-compound. G. F. M.

Preparation of a Bismethylhydrazinotetra-aminoarsenobenzene. C. F. BOEHRINGER & SÖHNE (D.R.-P., 285573; from *J. Soc. Chem. Ind.*, 1915, **34**, 1165).—When 3 : 5-dinitro-4-methylnitroaminobenzene-1-arsinic acid is reduced by means of stannous chloride at 50°, it yields the hydrazine *derivative*,

$$[NH_2\cdot NMe\cdot C_6H_2(NH_2)_2]_2As_2,$$

which has a pronounced trypanocidal action. J. C. W.

Physiological Chemistry.

The Controlling Influence of Carbon Dioxide. III. The Retarding Effect of Carbon Dioxide on Respiration. FRANKLIN KIDD (*Proc. Roy. Soc.*, 1916, **89**, [*B*], 136—156).—Previous work has shown that the resting-stage of the moist seed is primarily due to the narcotic action of carbon dioxide. It is now shown that the rate of anaërobic production of carbon dioxide is depressed by carbon dioxide; this passes off when the concentration of carbon dioxide is lowered. The same occurs in aërobic respiration; when the oxygen is deficient, carbon dioxide has no retarding effect. The production of carbon dioxide in both conditions is regarded as having a genetic relationship in normal respiration, the rate of the anaërobic process acting as the limiting factor. It is "floating respiration" (Blackman) which is retarded by carbon dioxide.

W. D. H.

The Action of Chlorine on the Blood. WILSON HAKE (*Lancet*, July 10, 1915).—The addition of chlorine to blood causes the absorption bands to disappear. A few bubbles of the gas renders the blood colourless, the filtrate being as clear as water. Chlorine water produces a brown filtrate. When chlorine is used, protein is precipitated, and this is destitute of colour. The iron goes into solution as a ferric salt.

W. D. H.

The Effect of Isotonic Ringer's Solution on Blood-corpuscles. F. H. SCOTT (*J. Physiol.*, 1915, **50**, 128—139).—Isotonic Ringer's solution and solution of sodium chloride are not indifferent liquids, but dissolve out from the corpuscles protein and non-protein nitrogen. The corpuscles are thus permeable to these two kinds of nitrogenous compound. The non-protein nitrogen is probably chiefly amino-acid and urea; the protein material dissolved is not precipitable by half saturation with sodium sulphate at 35°, but it is precipitated by trichloroacetic acid.

W. D. H.

The Time Required by Reduction of Oxyhæmoglobin in Vivo. D. FRASER HARRIS and H. J. M. CREIGHTON (*J. Biol. Chem.*, 1915, **23**, 469—470).—The oxyhæmoglobin bands seen in the red glare between adjacent fingers fade after bandaging the wrist in 18—26 seconds, and in the rabbit's ear in 40 seconds. Reductase in vitro requires more than 2 minutes.

W. D. H.

Blood-fat. II. Fat Absorption and the Blood Lipoids. W. R. BLOOR (*J. Biol. Chem.*, 1915, **23**, 317—326).—The fatty acids of the blood are increased in alimentary lipæmia, but the extent of the increase varies in different animals, and in the same animal at different periods, even when the amount and kind of fat are the same. Cholesterol variations are small and irregular, and

this substance takes at most a minor part in the phenomena of fat-absorption. Lecithin was increased in all experiments (average 20%), but this does not run exactly parallel with the fatty-acids. This favours Leathes' view that lecithin is a stage through which fats must pass before they can be utilised in metabolism; according to Leathes the synthesis occurs in the liver, and the presence of fat droplets in the liver during fat-absorption supports this. On the other hand, the passage of the fat *viâ* the thoracic duct into the general circulation appears to have for its object the avoidance of the liver altogether. It is, however, well known that the fat of the thoracic duct does not account for all the fat absorbed, so it is possible that the residue (30% to 40%) passes to the liver by the portal vessels, and d'Errico showed that during fat absorption portal blood is richer in fat than jugular blood. It is also possible that the intestine may synthesise lecithin as it does fat, but this view is not pressed. W. D. H.

Blood-fat in Relation to Heat Production and Depth of Narcosis. J. R. MURLIN and J. A. RICHE (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 7—8).—An emulsion of lard was introduced into the circulation of dogs; heat production rises, and the respiratory quotient falls, indicating that combustion of the fat takes place. Chloretone was given to ensure complete muscular rest, and it was found that the deeper the narcosis the more the blood-fat falls. As narcosis passes off, the heat production rises. Similar results were obtained with morphine. W. D. H.

The Acid-base Equilibria in the Blood after Parathyroidectomy. D. WRIGHT WILSON, THORNTON STEARNS, and MADGE DE G. THURLOW (*J. Biol. Chem.*, 1915, **23**, 89—121).—After parathyroidectomy in dogs, alkalosis may develop, which is neutralised by the acid products formed by the muscular activity incident to tetany, and after acute tetany, acidosis may be the ultimate result. Periodic variations in the "non-volatile" acid-base equilibrium seem to accompany the periodic attacks. The acidosis is associated with relief from tetany. Calcium salts, when injected into animals in tetany, lower the value of the dissociation constant of oxyhæmoglobin and the alveolar carbon dioxide pressure, an effect similar to that brought about by the introduction of acids.
W. D. H.

A Comparison of the Effects of Dextrose and Meat Feeding on the Non-protein Nitrogen of the Blood, and the Duration of Life in Experimental Renal Insufficiency. J. H. AUSTIN and S. S. LEOPOLD (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 3—4).—Renal insufficiency was produced in dogs by ligature of both ureters; some of these animals were given meat, the others dextrose. Forty-five hours later, the loss of weight in the dextrose animals was the greater, and the non-protein nitrogen of the blood lower. Sixty-nine hours after the operation, only one of the meat-fed dogs survived, whereas those in the dextrose group were all

alive; the lower nitrogen figure appears to be favourable for duration of life. W. D. H.

The Residual Nitrogen of the Blood. I. IVAR BANG (*Biochem. Zeitsch.*, 1915, **72**, 104—118).—A series of researches has been carried out by the author with the object of estimating the amino-acids and carbamide in the blood under various physiological and pathological conditions, for which purpose he has employed his own micro-methods, published in a monograph (Wiesbaden, 1915).

The content of amino-acid and nitrogen in the human subject lies between 3 and 22 mg. per 100 grams of blood, with a mean value of 12. The carbamide nitrogen lies between the numbers 6 and 20, with a mean value of 12. The total residual nitrogen averages about 25, with the extreme variations of 19 and 36 mg. The numbers obtained for ox-blood do not differ very greatly from those of the human subject; the few experiments made with the blood of sheep, pig, and horse yield substantially the same numbers. In the case of rabbits, on the other hand, the numbers found are appreciably higher. The total residual nitrogen yields the mean value of 33, with variations between 24 and 47; for carbamide nitrogen the mean is 16 (variations from 8 to 33), and for amino-acid nitrogen 17. The residual nitrogen of the corpuscles does not differ markedly from that of the plasma; the carbamide nitrogen is generally the same, and where there is a difference in the amino-acid nitrogen, the corpuscles in most cases contain more than the plasma. S. B. S.

The Residual Nitrogen of the Blood. II. IVAR BANG (*Biochem. Zeitsch.*, 1915, **72**, 119—128).—The residual nitrogen of rabbits' blood increases during starvation; the increase is due entirely to the larger amount of carbamide, as the content in amino-acids remains practically constant. The carbamide rapidly diminishes in amount after feeding. The increased amount of carbamide nitrogen in starvation in the blood is due to want of water, and can be prevented by administration of large amounts of liquid.

An increase in residual nitrogen in the blood (in dog and man) also results from a diet containing excessively large amounts of protein, which is also due only to an increase in the carbamide; the amino-acids, on the other hand, tend to diminish in quantity, and in some cases even entirely disappear. The alimentary "hypercarbamidæmia" is produced only after diets containing an excessively large quantity of proteins, and does not follow an ordinary mixed diet. It is of short duration only, and has generally completely disappeared after nine hours. S. B. S.

The Residual Nitrogen of the Blood. III. IVAR BANG (*Biochem. Zeitsch.*, 1915, **72**, 129—138).—Whilst the administration of moderate amounts of protein to rabbits does not produce an increase in the amino-acids in blood, this is not the case when the amino-acids themselves are given. The increase in the amino-

acids in the blood is observed about one hour after the administration. The increase is much more marked in fasting than in well-fed animals. A considerable amount of the amino-acid is excreted in the urine. The increase in the amino-acids in the blood following their ingestion is compared and contrasted with alimentary glycosuria. It is shown that the onset of the latter condition is much more rapid than the increase in the amino-acids of the blood. From the results of estimations of the amino-acids in the blood and in the urine after injection of glycine, the inference is drawn that the amino-acids are in part retained in the tissues, and are then gradually released and pass into the blood-stream. The increase of amino-acids in the blood of a dog after their ingestion is relatively small. In man, on the other hand, the increase is relatively large, as it is in the case of rabbits. S. B. S.

The Residual Nitrogen of the Blood. IV. IVAR BANG (*Biochem. Zeitsch.*, 1915, **72**, 139—145).—Experiments were carried out to determine the effects of the administration of carbamide. The most striking effect is the great toxicity of the substance, especially when administered to starving animals. A rapid rise in the amount of carbamide in the blood also follows the administration, which reaches its maximum in between one and two hours. This phenomenon is in marked contrast to the effect produced by amino-acids (see preceding abstract), where the increase in these acids in the blood is not observed until about two hours after their ingestion. Carbamide is not so toxic when administered intravenously. It is rapidly excreted by the kidneys, but a hypercarbamidæmia exists for some time, a fact which is taken to indicate that the kidneys become fatigued, and that the excretion of carbamide is an active secretory process and not a mere filtration. The experiments also indicate that carbamide is taken up by the tissues. The toxic symptoms produced by carbamide are described, and their similarity to those of uræmia and of ammonia poisoning is noted. An analysis of the blood of animals poisoned by carbamide shows that this fluid contains abnormally large amounts of ammonia, and the results leave little doubt that the carbamide is decomposed into ammonia, the latter substance being the true cause of the toxic effects. S. B. S.

The Residual Nitrogen of the Blood. V. IVAR BANG (*Biochem. Zeitsch.*, 1915, **72**, 146—168).—The effect of nephritis experimentally produced in rabbits by mercuric chloride, potassium chromate, and tartaric acid was studied.

A dose of 15 mg. of mercuric chloride is necessary to produce toxic symptoms in a well-nourished rabbit, whereas one-third of this dose is toxic to starving animals. In both cases the effect is accompanied by a large increase in the carbamide of the blood. There is no parallelism between this increase and albuminuria. In the case of the well-fed rabbits poisoned with large doses, it is conceivable that the hypercarbamidæmia was associated with starvation, as in this case animals refuse food after administration of the drug. As, furthermore, as has been already pointed

out by the author, starvation hypercarbamidæmia is connected with the want of water, numerous experiments were carried out to ascertain the effect of administration of water on the toxic symptoms produced by mercuric chloride. The results indicate that the retention of carbamide in the blood is not entirely or even primarily due to starvation. On the other hand, water has a considerable influence on the course of the intoxication. It appears that in order to produce injury to the kidneys, the drug must have a certain higher limit of concentration. When administered to a well-nourished animal with a plentiful store of water in the body, the drug is diluted as it passes through the kidney and produces a relatively small effect. On the other hand, when once the kidney has been injured by the action of mercuric chloride (passing through this organ in relatively high concentration, as would happen with large doses, or with small doses given to a starving animal), subsequent administration of water has little effect on the course of the toxic symptoms.

It is found, furthermore, that the ingestion of food after injury to the kidney produces some curative action. It has not yet been discovered what constituent of the diet produces this specific effect, but it is noticed that feeding caused a diminution of the hypercarbamidæmia, which is regarded as a measure of the efficiency of the organ.

The results of chromate nephritis were not so constant as those produced by mercuric chloride. They show also a marked want of parallelism between albuminuria and hypercarbamidæmia. Tartrate nephritis is similar to that produced by mercuric chloride.

Attention is called by the author to certain clinical aspects of his results. He also draws the conclusion that they support the secretion rather than the filtration theory of the action of the kidneys.

The effect of phosphorus poisoning is to produce a large increase of the amino-acids in the blood, accompanied by a relatively small increase of the carbamide. The animal dies from uræmia, which is ascribed to ammonia poisoning. Attention is called to the fact that all cases of uræmia cannot be ascribed to ammonia poisoning, although this is the probable cause of toxic symptoms in eclampsia and in phosphorus poisoning. S. B. S.

The Effect of Ingested Purines on the Uric Acid of the Blood. W. Denis (*J. Biol. Chem.*, 1915, **23**, 147—155).—In normal men no increase in the circulating uric acid is produced by the ingestion of large quantities of purines, but a rise occurs in cases of renal insufficiency. W. D. H.

The Action of Blood Serum after Intravenous Injection of Sucrose. F. Röhmann (*Biochem. Zeitsch.*, 1915, **72**, 26—100).—Details are given of numerous experiments which amplify the observations already published of the author and by Kumagai on the changes produced in the serum by the injection of sucrose (A., 1914, i, 766). They confirm the statement that the serum of

animals (rabbits and dogs) after parenteral administration of this sugar acquires the power of converting sucrose into dextrose and lævulose, and of converting these hexoses into lactose. This property is, however, only acquired after administration of large doses of sugar, and the results even then are not quite constant. The "passive immunisation" of animals is also confirmed. The relationship of these phenomena to those of ordinary protein immunisation are discussed. Details of experiments on about fifty animals are given in the paper. S. B. S.

Reduction of Oxyhæmocyanin in the Serum of Limulus polyphemus, L. CARL L. ALSBERG (*J. Biol. Chem.*, 1915, **23**, 495—503).—The view is advanced that the reduction which occurs in this serum on keeping, which is slow, is due to microbic action. W. D. H.

So-called Protective Enzymes. VIII. The Mechanism of Anaphylaxis and Antianaphylaxis. J. BRONFENBRENNER (*Proc. Soc. expt. Biol. Med. New York*, 1915, **13**, 19—21).—The interaction between an immune serum and its substratum or antigen leads to the formation of toxic fission products which originate from the serum itself. The serum normally contains proteolytic enzymes which require special conditions to exhibit their activity; normally their action is restrained by the colloids present, but *in vitro* one can alter the colloid concentration, thus diminishing the antitryptic (inhibiting) power and setting the enzymes free. One result of the interaction of antigen and its anti-substance is an influence on the colloidal conditions which allows the enzymes to act. In anaphylaxis this also takes place, and the antitryptic power of the serum falls; this allows the enzyme to act, toxic products are formed, and anaphylactic shock follows; the shock may be prevented by increasing the antitryptic power of the animal's serum. The introduction of the poisons in amounts insufficient to kill the animal is followed by the death of the tissues immediately affected, and the intercellular enzymes are set free. These enzymes, possibly with the aid of those thrown out by the surrounding fixed cells, blood-serum, and leucocytes, dispose of the dead material, and some of the fission products of digestion, together with some non-protein constituents (lipoids?) of these cells exert an antitryptic action and inhibit the activity of the proteolytic enzymes. The preliminary injection of the poison thus causes an increase in the protein fission products in the animals' circulation, and the resulting change in colloidal dispersion paralyses the activity of proteolytic enzymes which are liberated on the subsequent introduction of a lethal dose of the antigen into the sensitised animal. This theory makes active immunity and anaphylaxis part of the same process, the difference being only in the rapidity and extent of proteolysis induced by the specific combination of antigen with its anti-substance *in vivo*.

W. D. H.

The Ammonia of the Gastric Juice. HARRY L. HUBER (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 13—15).—The occurrence of ammonia in the gastric juice of men and dogs was noted by Carlson; in dogs with Pavlov stomachs the amount varied from 0·5 to 3·5 mg. per 100 c.c. of juice; this rises when ammonium chloride is added to the food or if ulceration is produced; if the dog refuses to eat, the amount is also increased. The figure in normal men was the same as in dogs; on a low protein diet the amount fell and the urinary ammonia rose; on a high protein diet the ammonia both in the juice and the urine rose. Excess of alkali in the food did not affect the ammonia of the juice, but that in the urine fell immediately; during ingestion of acid the juice ammonia remained normal, whilst that in the urine was increased. In twenty-six patients with gastric disturbances (supposedly ulcers) a rise in the ammonia of the juice was noted in only five (two of cancer and three of simple ulcer). W. D. H.

Gastro-intestinal Studies. XI. The Relative Digestibility of Lard and Hydrogenated Vegetable Oil. C. A. SMITH, RAYMOND J. MILLER, and PHILIP B. HAWK (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 13; *J. Biol. Chem.*, 1915, **23**, 505—511).—By examination of the fæces in two men, it appears that the two kinds of fat given are equally satisfactorily digested and utilised. W. D. H.

The Behaviour of Some Hydantoin Derivatives in Metabolism. III. Parabanic Acid. HOWARD B. LEWIS (*J. Biol. Chem.*, 1915, **23**, 281—285).—As parabanic acid does not yield its nitrogen by the urease method, metabolism experiments on its fate are now possible; these were performed on rabbits and a dog. No toxic symptoms followed its administration and no conversion of any significant amounts into urea took place. Perfusion experiments on the liver also showed no such conversion. Parabanic acid, therefore, is probably not an intermediary metabolic stage in the conversion of uric acid into urea. W. D. H.

The Metabolic Relationship of the Proteins to Dextrose. III. Formation of Dextrose from Human Proteins. N. W. JANNEY and N. R. BLATHERWICK (*J. Biol. Chem.*, 1915, **23**, 77—80).—The ratio of dextrose to nitrogen in the urine is not always a certain basis for calculating the amount of sugar formed from protein in the body. This does not apply to the observations of Benedict and Lewis on a case of phloridzin diabetes in the human subject; there the diet was free from carbohydrate and the D:N ratio was 3·6:1. About the same value is reported in severe diabetes mellitus. In the present experiments, phloridzinised dogs were fed on human muscle, and nearly the same figure obtained, namely, 3·4:1. Statements in the literature of much higher ratios, such as 5:1, can no longer be accepted.
W. D. H.

The Fate of Ingested Sodium Nucleate in the Human Subject. MAURICE H. GIVENS and ANDREW HUNTER (*J. Biol. Chem.*, 1915, **23**, 299—309).—Even though the purine nitrogen given is completely absorbed and promptly re-excreted, only a fraction reappears as uric acid. From this Schittenhelm argues that uric acid cannot be a terminal metabolic product in man, but that it must be transformed into some other compound, presumably urea, since the human organism is admittedly incapable of making allantoin from uric acid. If this is admitted, the present experiments show that the human "uricolytic index" must vary from 29 to 94. In the lower animals this index is almost a constant for the species; the more plausible explanation now suggested is that purines entering or liberated in the intestine undergo before absorption a varying degree of bacterial destruction.

W. D. H.

The Physiology of Nutrition of Domestic Animals, Especially of the Ox. WILHELM KLEIN (*Biochem. Zeitsch.*, 1915, **72**, 169—252). —An improvement in the Zuntz method for determination of the gaseous metabolism is described, and also a modification of the Tigerstedt method, by means of which mean values taken over longer and shorter periods of observation can be obtained. A method for the estimation of small amounts of combustible gases is also described. The three main methods for determination of the respiratory exchanges (those of Zuntz, Pettenkofer, and Regnault-Reiset) give results in concordance with one another. The energy balance of the organism, as calculated from the results of measurement of respiratory exchanges, agrees with that got by the chemical analysis of the ingesta and egesta. Calculations were made as to the amount of energy consumed in the process of chewing the cud and of digestion, and the results agree with those obtained by Pächtner and Dahm. The estimation of the respiration by the skin and intestine of ox was made, and found to amount to 14% of the total (of carbon dioxide). The energy consumed in the act of standing of the animals was also determined. The energy needs of the animal at different ages, as found from the experiments of the author and others, are shown to be nearly proportional to the body surface. The author calls attention to the practical value of the work on respiratory exchanges for agricultural and other purposes. S. B. S.

The Cause of the Loss of Nutritive Efficiency of Heated Milk. E. V. MCCOLLUM and MARGUERITE DAVIS (*J. Biol. Chem.*, 1915, **23**, 247—252).—Skim-milk powder loses much of its efficiency to promote growth after prolonged boiling, especially at 15 lb. pressure. Wheat embryo does not deteriorate from this point of view after the same treatment. Skim-milk free from protein also remains active, so does whey freed from albumin. Lactose contaminated with the water-soluble accessory after heating still behaves like the unheated product. Heating caseinogen in an autoclave at 15 lb. pressure for an hour destroys its bio-

logical value as a complete protein. Heated caseinogen and heated milk powder have little or no toxicity; the deterioration is due to a loss of value of the protein fraction of the ration through changes produced in the caseinogen. W. D. H.

The Dietary Deficiencies of Rice. E. V. McCollum and Marguerite Davis (*J. Biol. Chem.*, 1915, **23**, 181—230).—Polished rice cannot be made to induce growth by the addition of purified protein, growth-promoting fat, or salts. If the salt content of milk powder (or desiccated egg) plus dextrin is altered to imitate that in rice, there is no loss of growth promotion in the mixture. Polished rice even when employed to the extent of 80—90% in a growth-promoting food is harmless. Even 2% of a growth-promoting food mixture furnishes enough of an essential accessory to induce growth. This accessory, aside from that in butter-fat, is present in aqueous and alcoholic extracts of wheat embryo and egg-yolk; it is thermostable. The amount of aqueous extract (freed from protein) necessary to supply enough of this accessory carries nitrogen equivalent to about 1% of the total nitrogen of the ration; about one-third of this suffices in the case of the alcoholic extract. The accessory is not the same as that in butter; addition of 20% of butter-fat does not induce growth unless the other is present also; both must be present before growth can proceed. W. D. H.

The Essential Factors in the Diet During Growth. E. V. McCollum and Marguerite Davis (*J. Biol. Chem.*, 1915, **23**, 231—246).—The value of lactose in growth promotion is due to the fact that most preparations contain as an impurity the water-alcohol soluble accessory; the same is true for most preparations of caseinogen, and this substance is also usually contaminated with the fat-soluble accessory. A method is described of obtaining caseinogen free from both accessories. Both must be present in small quantities, but growth and prolonged maintenance are in some measure proportional to the amount supplied. W. D. H.

Studies on Growth. II. The Probable Nature of the Substance Promoting Growth in Young Animals. Casimir Funk and Archibald Bruce Macallum (*J. Biol. Chem.*, 1915, **23**, 413—421).—Neither butter nor purified butter (free from vitamine) promotes growth in pigeons or rats; the addition of yeast is, however, efficacious. Whether yeast without butter will produce normal growth in rats, and whether there are one or more compounds in the yeast which promote growth, are still under investigation. W. D. H.

The Resumption of Growth after Long-continued Failure to Grow. Thomas B. Osborne and Lafayette B. Mendel [with Edna L. Ferry and Alfred J. Wakeman) (*J. Biol. Chem.*, 1915, **23**, 439—454).—The capacity to grow can be retained and exercised at periods beyond the age when growth usually ceases. In albino rats this latter age is 300 days, but resumption may be induced at

550 days. Growth can also be normally stimulated after stunting due to underfeeding or to feeding on imperfect proteins. This resumption of growth under the influence of a suitable diet is accompanied by a restoration of the procreative functions. Further work is in progress. W. D. H.

The Relationship between the Content of the Perspiration in Chlorine and Nitrogen and the Diet. ELMER BERRY (*Biochem. Zeitsch.*, 1915, **72**, 285—302).—During work more urine is excreted, even with intense perspiration, than during rest; its specific gravity is, however, smaller, and on this fact diet exerts no influence. The urine excreted during work is less acid and less coloured than that excreted during rest. The nitrogen excreted is nearly proportional to the time both during work and during rest, and the form of diet is without influence on this factor. Urine excreted during rest nearly always contains a larger amount of nitrogen than that excreted during work. The excretion of chlorine during work is enormously increased. In 21% of the time during which work was performed, 40% of the total chlorine of a twenty-four hours' period was excreted. In other experiments even higher amounts were observed. Diet has no influence on this excretion. In spite of its lower specific gravity, the urine excreted during work always contains a higher percentage of chlorine than that excreted during rest. It appears that diet does not have an essential influence on the chlorine and nitrogen contents of the perspiration. From 2—5·6% of the total nitrogen and from 13—30% of the total chlorine excreted appear in the perspiration under the conditions of experiment described. S. B. S.

The Apparent Change of the Osmotic Pressure of the Cell-contents with the Osmotic Pressure of the Surrounding Medium. JACQUES LOEB and HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1915, **23**, 157—162).—The osmotic pressure of the contents of *Fundulus* eggs corresponds with a freezing-point depression of 0·76°, and is the same whether the eggs are fertilised or not. When the egg is washed or kept in solutions of different concentrations, the osmotic pressure of the expressed juice varies somewhat with the outer fluid. It must be assumed that the outside solution adheres to the meshes of the outer part of the membrane without entering the egg. W. D. H.

The Influence of Electrolytes on the Diffusion of Potassium out of the Cell and into the Cell. JACQUES LOEB and MCKEEN CATTELL (*J. Biol. Chem.*, 1915, **23**, 41—66).—Hearts (like *Fundulus* eggs) after being poisoned by potassium chloride recover quickly when placed in salt solutions; the efficiency of the salts used depends (1) on their concentrations within certain limits and (2) on the valency of the anion. *Fundulus* eggs stained with neutral-red do not give up the stain to distilled water, but they do so when a trace of acid or some salt is added. The diffusion out both of potassium and the dye presupposes their combination

with the colloidal anion of the membrane; this is counteracted by the presence of an excess of anions (especially bivalent and tervalent anions) in the outer solution or by a trace of acid. The colloid in the membrane which unites with the potassium or the dye is probably an amphoteric electrolyte which, through the addition of acid, is transformed into a salt, in the dissociation of which the colloid forms a cation which is no longer able to bind other cations. Previous immersion in distilled water delays the poisonous action of potassium; traces of the water must get into the membrane, and this acts as a barrier, blocking the further diffusion of potassium into the cell. W. D. H.

The Rôle of Electrolytes in the Diffusion of Acid into the Egg of Fundulus. JACQUES LOEB (*J. Biol. Chem.*, 1915, **23**, 139—144).—Salts inhibit the toxic action of acids on *Fundulus* embryos. This is a function of the anion as well as the cation. Thiocyanates, acetates, sulphates, and tartrates inhibit strongly; chlorides, bromides, and nitrates less; and iodides least. Calcium, strontium, and to a less degree magnesium, inhibit more strongly than univalent cations. The antagonistic action of the anions is due to retardation of the rate of diffusion of acid through the egg-membrane. In the adult fish tartrates and thiocyanates are too toxic to be of use in inhibiting the action of acids. W. D. H.

Calcium in Permeability and Irritability. JACQUES LOEB (*J. Biol. Chem.*, 1915, **23**, 423—430).—The variation in the amount of calcium or of calcium plus magnesium required to antagonise various concentrations of sodium chloride, or of that salt plus potassium chloride, was investigated both as regards permeability and irritability in barnacle larvæ. In regard to irritability, the calcium required varied in direct proportion to the concentration of salt (Weber's law), but in regard to permeability, the amount varied approximately with the square of the ratio of the concentration of the sodium chloride. W. D. H.

Xanthophyll, the Principal Natural Yellow Pigment of Egg-yolk, Body-fat, and Blood-serum of the Hen. The Physiological Relation of the Pigment to the Xanthophyll of Plants. LEROY S. PALMER (*J. Biol. Chem.*, 1915, **23**, 261—279).—The natural pigment of egg-yolk, body-fat, and blood-serum of the hen is physiologically identical with the carotin and xanthophyll pigments of plants, with the latter present in excess. In the cow, however, carotin is the predominating pigment of milk, serum, and adipose tissue. If xanthophyll is reduced in the hen's food, there is no appreciable decrease in the amount of pigment carried by the blood and deposited in the yolk. But if the rations are relatively free from both carotin and xanthophyll, this amount is much reduced. W. D. H.

The Action of Certain Inorganic Salts and Quinine on the Activity of the Mammalian Heart. F. B. HOFMAN and T. SAKAI (*Zeitsch. Biol.*, 1915, **66**, 293—325).—Diminution of the sodium

chloride in Locke's perfusion fluid to 0·5—0·2% (keeping it isotonic by the addition of sugar), causes the ventricle to become more excitable and contractile after the division of the auriculo-ventricular bundle; still further reduction of the salt stops the ventricle; the auricle acts similarly, but is more sensitive; if the heart is intact the auricles stop and the ventricles beat slowly. Increase of the potassium lessens excitability, and inhibits "extra systoles." In some cases there is a preliminary stage of increased frequency; under these conditions, the optimum of calcium is high, but varies. Quinine inhibits "extra systoles." W. D. H.

The Influence of Adrenaline on the Coronary Circulation of the Monkey. HENRY G. BARBOUR and ALEXANDER L. PRINCE (*J. expt. Med.*, 1915, **21**, 330—337).—The experiments were made on isolated hearts perfused with Locke's solution. In dog, cat, rabbit, ox, sheep, and pig the addition of adrenaline dilates the coronary vessels, but in the monkey constriction occurs; there is some evidence that man and monkey are alike in this particular, and the conclusion is drawn that in these two species the coronary arteries are supplied with vaso-constrictor nerves. W. D. H.

Vagus Stimulation of the Adrenalised Heart. M. KURODA and YAS KUNO (*J. Physiol.*, 1915, **50**, 154—156).—The cardiac vagus is rendered inexcitable by the injection of adrenaline; it is doubtful if this is due to a direct effect of adrenaline or to the increased intracardiac pressure which it causes. Bessmertny concluded in favour of the former, because "emostasin" raises the pressure as much as adrenaline, but does not affect the vagus. In the present experiments on the "heart-lung preparation," the pressure was raised by (1) increasing the venous supply, and (2) by adrenaline without any increase in the venous supply. Frequently vagus stimulation was ineffective when the arterial pressure was raised to less than twice its normal height by adrenaline. This abolition lasts longer than in the intact animal. W. D. H.

The Action of Caffeine and Adrenaline on the Vagus Nerve. HENRY G. BARBOUR and SIMON B. KLEINER (*J. Pharmacol. expt. Ther.*, 1915, **7**, 541—544).—Both drugs accelerate the heart, but this may be masked by central stimulation of the vagus. If the vagi are cut, increase of the heart's rate is always obtained. When either is perfused through the frog's heart, vagus stimulation usually produces no inhibition; after caffeine, recovery is more complete than after adrenaline. The effect of adrenaline is due to depression of the vagus endings in the heart; this may be partly true for caffeine, but here there is an additional factor, namely, increased irritability of the cardiac muscle. W. D. H.

The Action of Phenylethylamine on the Heart. HENRY G. BARBOUR and EDWARD M. FRANKEL (*J. Pharmacol. expt. Ther.*, 1915, **7**, 511—527).—Phenylethylamine is a cardiac poison, in small amounts stimulating, and in large amounts depressing the

mammalian heart. In the frog the stimulating effect does not occur. It also stimulates constriction of the coronary arteries. The effects are reversible, and disappear on perfusion with Clark's or Locke's modification of Ringer's solution. W. D. H.

The Production of Atrio-ventricular Rhythm in Man after the Administration of Atropine. FRANK N. WILSON (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 17—18).—Several types of disturbed cardiac rhythm were observed in men (both healthy and affected with heart disease) after a dose of atropine, which are explained by assuming that this drug releases the *A-V* tissues from vagus control before it releases the sinus node. W. D. H.

The Action of Heavy Metals on the Isolated Intestine. WILLIAM SALANT and C. W. MITCHELL (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 15—16).—Very low concentrations of zinc salts depress the muscular activity of the intestine (Magnus's method); some recovery occurs in Locke's solution unless the injury is too pronounced. Nickel acetate produces temporary depression, followed by recovery and sometimes stimulation. Recovery even after strong solutions is complete in Locke's solution. The reaction to pilocarpine and to barium in these experiments points to more resistance in the muscle fibres than in the nerve-endings. W. D. H.

The Response of the Surviving Uterus to Morphine and Scopolamine. HENRY G. BARBOUR and NAT H. COPENHAVER (*J. Pharmacol. expt. Ther.*, 1915, **7**, 529—539).—Morphine (0·05 to 0·01%, and sometimes 0·002%) stimulates the isolated uterus of cat and guinea-pig to an increase of tone. Scopolamine acts in the same way, but is ten times more powerful. Inhibitory effects with large doses, as described by Kehrer, were not obtained. W. D. H.

The Action of Morphine and Scopolamine on the Intact Uterus. HENRY G. BARBOUR (*J. Pharmacol. expt. Ther.*, 1915, **7**, 547—555).—In the intact animal (decerebrated), morphine and scopolamine cause a temporary increase of tone in the pregnant or non-pregnant animal. That large doses inhibit is not due to their action on the uterus itself, but any delay in labour they produce is due entirely to their cerebral action. W. D. H.

The Occurrence of Pituitrin and Adrenaline in Fœtal Pituitary and Suprarenal Glands. CAREY PRATT MCCORD (*J. Biol. Chem.*, 1915, **23**, 435—438).—Bovine organs were used, and the extracts were physiologically active during all developmental stages in which the suprarenal and pituitary glands were microscopically recognisable; for the pituitary this is from the eighth week, and for the suprarenal from the sixth week of intra-uterine life. The fœtus is thus not merely under the influence of the maternal internally secreting organs. W. D. H.

Failure of Pituitrin to Sensitise the Sympathic System. R. G. HOSKINS (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 16—17).—Kepinov states that small quantities of pituitary extract "sensitise" the point of attack of adrenaline (the sympathetic endings), so that small doses of the latter will thus produce large effects. The present experiments fail to support this contention.

W. D. H.

The Influence of Pancreatic Extracts on the Production of Lactic Acid in Surviving Muscles. GEORGE WINFIELD and F. GOWLAND HOPKINS (*Proc. physiol. Soc.*, 1915, v—vi; *J. Physiol.*, **50**).—Pancreatic extracts were added to minced muscle, and the yield of lactic acid compared with that in similar preparations without such additions. Those with the added extract showed less lactic acid. This inhibitory action is not confined to the action of the pancreas on the autogenous muscle, but is produced by preparations from widely different sources. The responsible factor is thermostable, and is thus similar to Cohnheim's glycolytic factor.

W. D. H.

Biochemistry of Iodine. II. The Distribution of Iodine in Plant and Animal Tissues. A. T. CAMERON (*J. Biol. Chem.*, 1915, **23**, 1—39).—Iodine is always present in marine algæ between the limits of 0·001% and 0·7%. Land plants contain much less; all sea animals contain iodine. As one rises in the animal kingdom differentiation occurs, and the iodine is localised in certain organs, and the total in the whole system becomes less. Full details are given for sponges, corals, worms, ascidians, and molluscs. In ascidians, the endostyle, which represents the thyroid, contains iodine, but less than the thyroid of vertebrates does. In vertebrate tissues the thyroid alone is important as a storage place for iodine, the percentage in the dry tissue varying from 0·01 to 1·16. Other tissues contain less than 0·001%, except in the liver and kidney of fishes, where the amount is slightly higher. Variations in the iodine content of the thyroid can all be traced to differences in diet. In elasmobranch fish there is no evidence that the thyroid tissue of females contains more iodine than the male tissue.

In the analyses Kendall's method was used. W. D. H.

The Non-destructibility of Uric Acid in the Human Organism. MORRIS S. FINE (*J. Biol. Chem.*, 1915, **23**, 471—473).—Contrary to the findings of Schittenhelm and Wiener, the present analyses show that uric acid can be demonstrated in considerable concentrations in human tissues; the contention of these workers that human tissues decompose uric acid is not supported.

W. D. H.

The Salts Required for the Development of Insects. JACQUES LOEB (*J. Biol. Chem.*, 1915, **23**, 431—434).—The experiments show that an animal as highly organised as the banana fly can be raised on a culture medium as simple as that required by certain micro-

organisms; the liquid used contained dextrose, sucrose, ammonium tartrate, citric acid, dipotassium hydrogen phosphate, and magnesium sulphate dissolved in water. W. D. H.

The Preparation of Protein-free Milk. H. H. MITCHELL and R. A. NELSON (*J. Biol. Chem.*, 1915, **23**, 459—467).—The protein is removed by trichloroacetic acid; preliminary experiments indicate that such protein-free milk may be used with advantage as a basis of the ration in metabolic work. W. D. H.

The Action of Animal Extracts on the Flow of Bile. ISAAC OTT and JOHN C. SCOTT (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 12).—In etherised cats, equal doses of secretin cause equal increments in the flow of bile. Animal extracts were then added to the secretin; extracts of parathyroid, mammary gland thyroid, and corpus luteum have little or no effect; the flow is increased by extract of tonsil and decreased by adrenaline, pituitrin, and extracts of pancreas and of thymus. W. D. H.

The Reaction of Bile. SEIZABURO OKADA (*J. Physiol.*, 1915, **50**, 114—118).—The reaction of bile from the gall-bladder and from the liver is different, the former being more variable and inclining more to the acid side; liver bile is alkaline; its H·-ion concentration is $1{\cdot}5 \times 10^{-8}$ at 23°; it turns red lacmoid blue, but does not turn phenolphthalein red. The reaction of bile from the liver during digestion corresponds with that of pancreatic and intestinal juices and with the optimal point for trypsin, pancreatic lipase, and erepsin. W. D. H.

The Excretion of Acids and Ammonia after Parathyroidectomy. D. WRIGHT WILSON, THORNTON STEARNS, and J. H. JANNEY, jun. (*J. Biol. Chem.*, 1915, **23**, 123—137).—After parathyroidectomy in dogs, there is usually a sudden diminution in the excretion of acids and ammonia and a decrease in the ammonia ratio and the hydrogen ion concentration of the urine. With the development of tetany, the elimination of acids and ammonia increases, and the ammonia ratio and hydrogen-ion concentration rises. This indicates that the alkalosis resulting from the operation is neutralised by the development of tetany. After acute or chronic tetany acidosis may occur. W. D. H.

The Chlorides in Diabetes after Pancreatectomy. JAMES ELAZER LEBENSOHN (*J. Biol. Chem.*, 1915, **23**, 513—520).—Chloride metabolism in dogs after removal of the pancreas remains normal; so also does the permeability of the intestine as regards the absorption of chlorides. W. D. H.

The Supposed Acid Intoxication of Diabetic Coma. E. P. POULTON (*Proc. physiol. Soc.*, 1915, i—iii; *J. Physiol.*, **50**).—In the acidosis of carbohydrate starvation, the hydrogen-ion concentration of the blood remains constant, for the increase in acid

is compensated for by lessening of carbon dioxide; but the question is open whether in the severe type of acidosis in diabetes this holds good; the general belief is that acid intoxication occurs. The present observations were on eight patients with varying severity of the symptoms. When the coma was deep (two cases), the hydrogen-ion concentration was distinctly higher than normal, but the fact that in the other cases where there was definite drowsiness, the blood reaction was normal, argues against diabetic coma being due to acid intoxication. After severe muscular exercise the acidity of the blood is greater than in the depth of diabetic coma, but there are no signs of acid intoxication.

W. D. H.

Experimental Study of Fever. JUDAH LEON JONA (*J. Hygiene*, 1916, **15**, 169—194).—A definite rise of body temperature occurs in rabbits after injecting a minute amount (0·00004 gram) of cultures of *Bacillus coli communis* or *B. typhosus* in Ringer's solution. Larger doses cause collapse and even death. The substances to which this is due are soluble in water and saline solutions, insoluble in ether and in alcohol. Their potency is lessened by contact with alcohol. They may be separated from the solutions by filtering through a collodion filter. They are therefore colloidal or adherent to colloid materials. They are not destroyed by boiling or by dry heat at 110°. The fever lasts a few hours, and is due to diminution in the loss of heat; heat production is unaffected or may be increased. The fall of temperature in collapse is accompanied by decrease of both production and loss of heat. In animals in which the brain stalk has been severed distal to the optic thalamus, no fever was caused after the injection of the ordinary pyretic dose. W. D. H.

Icterus. A Rapid Change of Hæmoglobin into Bile-pigment in the Pleural and Peritoneal Cavities. C. W. HOOPER and G. H. WHIPPLE (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 22—23).—The introduction of solutions of hæmoglobin into the blood-vessels of dogs the livers of which have been excluded from the circulation, is followed by a prompt formation (within two hours) of bile pigment in which the liver can have no part. The same is true when the hæmoglobin is introduced into the pleural or peritoneal cavities. The endothelial linings are probably responsible for the transformation; the power may be, however, a general property of all protoplasm. W. D. H.

Potassium in Normal and Nephropathic Kidney Cells. WM. DEB. MACNIDER (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 10—12).—Potassium was determined microchemically by Macallum's method in dogs. Normally the kidney cells show only traces, the nuclei possessing none. In nephritis produced by uranium nitrate the amount rises, and some is present in the nucleus; this is most marked in the cells of the convoluted tubules.

W. D. H.

The Interpretation of a Positive Nitrogen Balance in Nephritis. HERMAN O. MOSENTHAL (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 9—10).—Retention of nitrogen in nephritis is usually due to renal insufficiency, but the present results show that this is not necessarily followed by a rise in the non-protein nitrogen of the blood. W. D. H.

Uric Acid, Urea, and Creatinine of the Blood in Early and Late Nephritis. V. C. MYERS, M. S. FINE, and W. G. LOUGH (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 5).—In early nephritis the blood resembles that found in gout in a rise of uric acid, but as the disease progresses and the permeability of the kidney is lowered, the urea rises, and lastly the creatinine follows suit; the rise in creatinine may near death be twenty times the normal. W. D. H.

The Action of Barium Chloride on the Circulation; the Antagonistic Action of Nicotine and Curare. E. P. CATHCART and G. H. CLARK (*J. Physiol.*, 1915, **50**, 119—127).—The antagonistic action of nicotine and curare in skeletal muscle (Langley) holds good also for the muscular tissue of the arterioles. Nicotine inhibits or abolishes the rise of blood-pressure produced by barium chloride; curare then restores, or may even intensify, its pressor action. Barium chloride probably does not act on the muscle itself, but it acts on a different part of the apparatus from that on which adrenaline acts. W. D. H.

The Pharmacological Action of Tetra-alkyl Ammonium Compounds. II. and III. C. R. MARSHALL (*Trans. Roy. Soc. Edin.*, 1915, **50**, 379—398; 481—516).—II. The most prominent symptoms produced on frogs by the action of tetraethylammonium chloride are the following. The injection into the dorsal lymph sac produces muscular contractions and tremors. These symptoms are accompanied by some loss of co-ordination, a varying degree of paralysis with diminution or absence of reflexes or cessation of the respiratory movements. Doses of 2 mg. per gram of body-weight are lethal. The lethal dose for rabbits was found to be about 0·05 gram per kilo. of body-weight. The injection of 0·1 gram per kilo. into the ear vein produced at first deep convulsive breathing, followed by convulsive movements and paralysis of the hind limbs; the heart became weaker and weaker. The action of the drug on isolated nerve and muscle was studied in detail. Both muscular contractions and paralysis were found to be peripheral in origin. The tremors can be inhibited by the action of calcium salts when these are perfused through the animal (frog). Immersion of isolated muscle in a solution (1 in 1000) produces contracture, which is due to the presence of free acid in the commercial sample of the drug employed. The drug produces increased irritability or paralysis on the motor nerve-endings of mammals, the effect varying with the magnitude of dose and method of injection. In contradistinction to tetramethyl-

ammonium chloride, tetraethylammonium chloride exerts no distinctive action on the circulation. Injections produce a transient fall of blood-pressure in rabbits, the amount of which varies with the dose; this fall appears to be due to a vascular effect. In cats the effect is less than that in rabbits. The effect on the respiration in mammals is also comparatively small, and is much below that produced by tetramethylammonium chloride.

III. The relative pharmacological actions of the various methylethylammonium compounds are compared. The methylethylammonium compounds have actions intermediate between those of the tetraethyl and tetramethyl derivatives. When injected into the dorsal lymph-sac of frogs, trimethylethylammonium chloride produces paralysis and, rarely, a few muscular twitches. Dimethyldiethylammonium chloride produces chiefly paralysis, but there is distinct evidence of increased irritability of the nerve-endings. Methyltriethylammonium chloride caused slight irregular muscular movements and tremors, followed, when sufficient doses were given, by paralysis. The effect on tadpoles was similar to that on frogs. When tested on the mammalian circulation, the following were the broad effects produced. Methyltriethylammonium chloride is similar to, but slightly more powerful than, the tetraethyl compound, whereas trimethylethylammonium chloride is similar to, but less powerful than, tetramethylammonium chloride, which, as mentioned in previous communications, has a more marked action on the respiration and circulation than the corresponding ethyl derivative. The dimethyldiethyl compound has an intermediate action. The effects of these drugs on the isolated muscle of frog have been investigated in detail, and are illustrated by numerous tracings. In conclusion, attention is called to the fact that the most important action of quaternary ammonium compounds is on the myoneural junction, and the mode of action is fully discussed by the author. S. B. S.

The Elimination of Picric Acid by the Urine. M. MURAT and J. DURAND (*J. Pharm. Chim.*, 1916, **13**, 18—23).—Picric acid is but little toxic; doses of 1 gram are well borne, and except for a slight feeling of fatigue produce no symptoms. The colour of the urine resembles that in jaundice; elimination begins six hours after the dose and continues for about twelve days. The smallest dose necessary to produce the pseudo-icterus is 0·2 gram.

W. D. H.

Mercuric Chloride Poisoning in Animals Treated Unsuccessfully by Hall's Antidote. HENRY G. BARBOUR (*J. Amer. Med. Assoc.*, 1915, **64**, 736).—W. A. Hall recently suggested the treatment of cases of mercuric poisoning by a reversal of Mayer's reaction, namely, the employment of an alkaloid dissolved in potassium iodide solution which would precipitate mercuric chloride. In the present experiments quinine was selected as the alkaloid, and appropriate doses were given subcutaneously to mice and rabbits poisoned with mercuric chloride; the treatment was quite ineffectual. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

A Colorimetric Method of Adjusting Bacteriological Culture Media to any Optimum Hydrogen Ion Concentration. S. H. HURWITZ, K. F. MEYER, and Z. OSTENBERG (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 24—26).—The method involves the use of phenolsulphonephthalein as indicator and standard phosphate mixtures for comparison. If necessary, the hydrion concentration of the medium must be subjected to a preliminary rough adjustment so as to bring it between the limits $H^- = 6{\cdot}4$ and $H^+ = 8{\cdot}4$.
H. M. D.

Primary Changes of the Hexoses in Alcoholic Fermentation. H. EULER and E. HILLE (*Bied. Zentr.*, 1915, **44**, 575—576; *Zeitsch. Gärungsphysiol.*, 1915, **3**).—It was found that the decrease during fermentation, as indicated by the optical method, failed to agree with the amount of carbon dioxide produced, and the conclusion was drawn that a compound intermediate between glucose and carbon dioxide was formed. Attempts to obtain an intermediate compound by suppressing the second reaction by antiseptics and by heat failed to give the desired results. In presence of antiseptics, the intermediate product is used up as quickly as it is formed, whilst the reaction is stopped altogether by slightly heating.
N. H. J. M.

Production of Lactic Acid in Fermentation. OTTO BÜRGER (*Bied. Zentr.*, 1916, **45**, 72; *Centr. Bakt.*, ii, **43**, 245. Compare Moutang, *Zeitsch. ges. Brauwes.*, 1913, No. 24).—Dilute solutions of maltose, lævulose, and dextrose were fermented with pure yeast, and the acid estimated with *N*/20 barium hydroxide. The barium salt, like barium lactate, dissolved in alcohol.
N. H. J. M.

Vegetable Oxidation Ferments. O. BEGEMANN (*Biol. Zentr.* 1915, **44**, 547—548; *Zeitsch. allg. Physiol.*, 1914, **16**, 352—358). —Oxidation ferments were found in all the plants which were examined. Direct oxydases were found in the living cells, but not catalase and peroxydase. The influence of temperature and of light was investigated. The methods employed are described.
N. H. J. M.

Plant Ferments. IV. The Invertase of Potato Leaves. P. DOBY (*Biochem. Zeitsch.*, 1915, **71**, 495—500).—The presence of invertase in potato leaves was confirmed. The degradation of sugar by the ferment is a unimolecular reaction, and the velocity constant is proportional to its concentration. The juice expressed by low pressure is more powerful as regards invertase action than that expressed by high pressures. The reason for this phenomenon has not yet been ascertained.
S. B. S.

The Complex Carbohydrates and Forms of Sulphur in Marine Algæ of the Pacific Coast. D. R. HOAGLAND and L. L. LIEB (*J. Biol. Chem.*, 1915, **23**, 287—297).—The carbohydrates of *Macrocystis pyrifera* and *Iridaea laminarioides* were investigated. From the acid-precipitate complex known as "algin" a pentosazone closely resembling *l*-xylosazone was prepared; in the alcohol-insoluble carbohydrate fraction of *Macrocystis*, a methyl pentose having the properties of fucose is present; a similar fraction from *Iridaea* yielded only galactose. Marine algæ as exemplified by *Ulva fasciata* have a high sulphur content, and estimations are presented of the sulphur held in various forms. W. D. H.

Plant Chemistry. P. Q. KEEGAN (*Chem. News*, 1915, **112**, 295—296).—Qualitative organic analyses of hair moss (*Polytrichum commune*), early purple orchis (*O. mascula*), and marsh marigold (*Caltha palustris*), estimations of ash, and of calcium, magnesium, phosphoric acid, sulphates, and chlorides in the ashes. N. H. J. M.

Microchemistry of Plants. I. A Readily Crystallisable Tannin in Dionæa muscipula. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1915, **33**, 447—451).—The stems and roots of *Dionaea muscipula* contain a crystalline tannin which can readily be obtained by treating sections with glycerol, with concentrated solutions of sugar, or with diluted mineral acids. N. H. J. M.

The Measurement of Toxicity. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1915, **23**, 67—70).—Toxicity is recommended to be measured by ascertaining the electrical conductivity of living tissues. Instead of determining the time necessary to cause death, which the curves show is approached asymptotically, the criterion selected should be some convenient point on the curve, for example, when half-way between the normal state and death is reached. It is also desirable to select a standard temperature for the observations. The action of a large number of toxic substances follows the course of a unimolecular reaction. W. D. H.

Principles of Crop Production. EDWARD JOHN RUSSELL (T., 1915, **107**, 1838—1858).—A lecture delivered before the Chemical Society on November 18th, 1915. J. C. W.

The Identity of the Proteins Extracted from Wheat-flour by the Usual Solvents. C. H. BAILEY and M. J. BLISH (*J. Biol. Chem.*, 1915, **23**, 345—357).—Extracts of flour with 1% solution of sodium chloride contained a large proportion (more than half) of gliadin in the total protein present. Ten per cent. solution of this salt, or 5% solution of potassium sulphate, contained about 15% of protein in the form of gliadin; 50% alcohol extracts more gliadin than 30% or 70% alcohol, and the extraction is not complete unless the temperature is raised to 83° for three hours; in these extracts 93% of the nitrogen is present as gliadin. The amount of

non-gliadin proteins extracted by 50% alcohol was constant, regardless of their amount in the flour. The separation of gliadin from non-gliadin proteins by heat coagulation was not quantitative, considerable amounts of gliadin not being coagulated by boiling.

W. D. H.

Influence of Potassium Ferrocyanide on the Growth of Plants. E. HASELHOFF (*Bied. Zentr.*, 1915, **44**, 474—475; *Landw. Jahrb.*, 1914, **47**, 338).—The results of pot experiments with beans in which potassium ferrocyanide (0·5 and 1 gram) was added to the soil (25 kilos.) showed that in a loam soil the production of both seed and straw diminished, whilst in a sandy soil only the yield of straw was reduced.

In water-culture experiments, also with beans, the results were less definite. It was, however, shown that the toxic action of potassium ferrocyanide begins when the solution contains 0·1—0·5 gram per litre, and that the latter amount is strongly toxic.

N. H. J. M.

Action of Sulphur on Plant Production. TH. PFEIFFER and W. SIMMERMACHER (*Bied. Zentr.*, 1916, **45**, 18—20; *Fühling's Landw. Zeit.*, 1915, **64**, 243).—Application of sulphur to oats grown in plots on a soil containing plenty of organic matter failed to increase the yield and the amount of nitrogen taken up. Similar results were obtained with sugar-beet grown on the same soil without further applications of sulphur. N. H. J. M.

Relation of Sulphur to Soil Fertility. O. M. SHEDD (*Kentucky Exper. Station, Bull.* 188, Dec., 1914).—The results of soil culture experiments showed that addition of sulphur and calcium sulphate resulted in a decided increase in the yields of tobacco, soja beans, and turnips, whilst clover did not seem to be benefited. In the case of beans, the best results were obtained with sulphur. Several sulphates gave good results with mustard, and in some cases with radishes.

In sand cultures with lucerne, the best results were obtained with magnesium, iron, sodium, potassium, and ammonium sulphates, and good results were obtained with sulphur.

When sulphur is employed, the soil must contain calcium carbonate in order to neutralise the acidity produced by oxidation.

N. H. J. M.

Adsorption Power of Soil. II. PAUL ROHLAND (*Bied. Zentr.*, 1915, **44**, 575; *Internat. Mitt. Bodenk.*, 1915, **5**, 102).—The red soil is a silicate which, in contact with water, forms numerous colloids, as is shown by its power of adsorbing complex dyes, such as aniline-red, aniline-blue, methyl-violet, etc. As in the case of clay soils, the adsorptive power of the red soils is greater with blue and violet dyes than with red and green dyes, and least with brown and yellow dyes. The colorimetric method can accordingly be employed for estimating the colloids of red soils.

N. H. J. M.

Organic Chemistry.

Process for Accelerating and Assisting the Fixation of Acetylene in Chemical Reactions Requiring the Presence of a Catalyst. G. BOITEAU (Fr. Pat. 475853; from *J. Soc. Chem. Ind.*, 1916, **35**, 72).—The fixation of acetylene takes place more quickly and completely, and with less tendency to form tarry matters, when the catalyst is formed in presence of the reacting substance. Thus in the preparation of ethylidene diacetate from acetic acid and acetylene, instead of adding mercuric sulphate as such, it is formed by dissolving the oxide in the acetic acid and then adding the requisite quantity of sulphuric acid. G. F. M.

Interaction of Methylene Iodide and Silver Nitrate. C. R. MARSHALL and ELIZABETH GILCHRIST (*Proc. Roy. Soc. Edin.*, 1915, **35**, 227—231).—When methylene iodide is mixed with an equimolecular quantity of alcoholic silver nitrate solution, a crystalline precipitate of the composition $AgNO_3,CH_2I_2$ separates almost immediately (compare Scholl and Steinkopf, A., 1907, i, 116; Donnan and Potts, T., 1910, **97**, 1895). For the formation of this substance, the silver nitrate solution should not be weaker than decinormal, and gives the best results when saturated. The crystalline product, which is best preserved under an alcoholic solution of silver nitrate, decomposes slowly in the air, giving a residual mixture of silver iodide and silver nitrate. When heated, it decomposes at 79—80° with evolution of iodine and nitrous fumes. Water causes decomposition, with formation of nitric acid, formaldehyde, formic acid, and silver iodide, together with some of the unaltered constituent substances, the change being facilitated by the addition of an alkali hydroxide. Potassium cyanide solution effects the liberation of the methylene iodide with simultaneous formation of potassium argentocyanide.

From the fact that in alcoholic solution the conductivity of the above additive compound does not differ materially from that of the corresponding solution of silver nitrate, it appears probable that in alcoholic solution the substance is almost entirely resolved into its constituents. D. F. T.

Esters of *tert.*-Trichlorobutyl Alcohol and their Pharmacology. R. WOLFFENSTEIN, A. LOEWY, and M. BACHSTEZ (*Ber.*, 1915, **48**, 2035—2043).—The idea of administering a phenol in the form of an ester which slowly hydrolyses in the alkaline fluid of the intestine has occasionally been extended to alcohols. It has been assumed that, just as the corrosive action of a phenol can be masked and the pharmacodynamical value be slowly and continuously brought out by using an ester, so the esters of alcohols would have an additional pharmacological advantage over their components. As a matter of fact, however, such compounds as the

nitrate and acetate of glycerol are known to act quite differently from either component, and as most alcohols are so indifferent in themselves, they can scarcely be expected to lend any typical activity to their esters. The authors have therefore studied a number of esters of *gem.*-trichloro-*tert.*-butyl alcohol, $OH·CMe_2·CCl_3$, which is a powerful narcotic. It is found that most of the esters are unchanged in the organism, however, and that they frequently have a totally different action from the alcohol, usually causing convulsions.

gem.-Trichloro-*tert.*-butyl alcohol is remarkable in many chemical respects. It seems very indifferent towards dehydrating agents, sulphuric acid decomposing it like a hydroxy-acid, namely, with the evolution of carbon monoxide. Like chloral, it restores the colour to Schiff's reagent, and forms a hydrate. No sodium compound is known, and an attempt to prepare one, using the granulated metal, resulted in an explosion.

The esters were usually made by the interaction of the acid chloride and the alcohol in the presence or absence of a tertiary base, but some could be obtained by merely warming the acid and the alcohol together. *gem.*-Trichloro-*tert.*-butyl acetate,

$$CCl_3·CMe_2·OAc,$$

was described by Willgerodt and Dürr under the name "acetoxy-butyric trichloride" (A., 1889, 690). It is less narcotic, but more toxic than the alcohol. The *propionate* is a pale yellow oil, b. p. 88—90°/14 mm., and is still less narcotic; the iso*valerate*, b. p. 108—110°/20 mm., is a non-narcotic convulsant; the *bromo*iso-*valerate*, $CHMe_2·CHBr·CO_2·CMe_2·CCl_3$, b. p. 152°/17 mm., is a convulsant; the *chloroacetate*, m. p. 48°, and the *trichloroacetate*, long needles, m. p. 40°, are less active than the acetate. The *diethylaminoacetate*, $NEt_2·CH_2·CO_2·CMe_2·CCl_3$, prepared from the chloroacetate by the action of diethylamine, is an oil, b. p. 142—145°/20 mm., which forms a crystalline hydrochloride and a *platinichloride*, platelets, m. p. 212°; the *dimethylaminoacetate* also forms a *hydrochloride*, rhombic plates, m. p. 220°; both esters are powerful narcotics. The *piperidylacetate*,

$$C_5H_{10}N·CH_2·CO_2·C_4H_6Cl_3,$$

is a very bitter oil, and is a convulsant and not a narcotic. The *allophanate*, $NH_2·CO·NH·CO_2·C_4H_6Cl_3$, m. p. 114°, is also a convulsant, although most allophanates are narcotics. The *hydrogen malonate*, $CO_2H·CH_2·CO_2·C_4H_6Cl_3$, six-sided platelets, m. p. 116°, and the *malonate*, m. p. 102—103°, are remarkable in that they are not toxic or narcotic, but lower the threshold of excitation. The *αβ-dibromo-β-phenylpropionate*, $CHPhBr·CHBr·CO_2·C_4H_6Cl_3$, m. p. 99—100°, is almost indifferent. J. C. W.

Etherates of Magnesium Haloids. N. Domanicki (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1790—1792).—Etherates of magnesium bromide and iodide were prepared by Menschutkin (A., 1904, i, 215). Magnesium chloride forms a *monoetherate*, $MgCl_2,Et_2O$, which is obtained in white, acicular crystals, turning black and decomposing when heated, by the action of magnesium on either

an ethereal solution of $\alpha\beta$-dichloroethane or a mixture of dry ether with sulphur chloride, $Mg + S_2Cl_2 + Et_2O = MgCl_2,Et_2O + S_2$. *Magnesium chlorobromide monoetherate*, $MgClBr,Et_2O$, is obtained by the action of magnesium on an ethereal solution of α-chloro-γ-bromopropane. A similar compound of magnesium chloro-iodide could not, however, be obtained, probably because magnesium chloride forms only a mono-etherate and magnesium iodide only a di-etherate. T. H. P.

Kephalin. II. Brain Kephalin. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1916, **24**, 41—53. Compare Levene and West, A., 1914, i, 12).—The discrepancy between the formula of kephalin as calculated from the identified constituents (compare Parnas, A., 1910, i, 4; 1913, i, 1253; Baumann, A., 1913, i, 1041; Renall, A., 1913, i, 1254) and the results of analysis appear to indicate either the presence of impurity or the existence of a constituent which has hitherto escaped detection.

By submitting kephalin to treatment with various solvents, it was not found possible to alter the composition of the phosphatide, the analytical results agreeing with a formula $C_{41}H_{78}O_{13}NP$, whereas the hydrolytic products suggest $C_{41}H_{78}O_8NP$. Conversion into, and recovery from, the lead salt also failed to effect any change in the composition of the original material. It is therefore probable that so-called kephalin contains some other substance in addition to the recognised components kephalinic acid, stearic acid, aminoethyl alcohol, glycerol, and phosphoric acid. The constituent which is unaccounted for may not form an essential portion of the molecule, but may be a very persistent impurity.

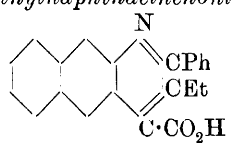
By reduction of a solution in a mixture of ether and acetic acid, with hydrogen and colloidal palladium, kephalin is reducible to *hydrokephalin*, an almost colourless, amorphous powder. D. F. T.

Glyceryl Ester of Tetrachlorotetraiodoterapic Acid. JOSÉ J. CERDEIRAS (*Anal. Fis. Quim.*, 1915, **13**, 439—441).—A substance isolated from cod-liver oil proved on analysis to be the glyceryl ester of tetrachlorotetraiodoterapic acid, $C_3H_5(C_{17}H_{23}O_2Cl_4I_4)_3$. A. J. W.

Syntheses by means of Mixed Organometallic Derivatives of Zinc. Method of Preparation of α-Ketonic Acids. E. E. BLAISE (*Bull. Soc. Chim.*, 1915, [iv], **19**, 10—18. Compare Bouveault and Locquin, A., 1904, i, 551, 847, 848; 1905, i, 10).—α-Ketonic acids can be prepared by the following series of reactions. Ethyl oxalyl chloride is condensed with α-hydroxy*iso*butyric acid, and the crude acid product converted into its acid chloride by means of thionyl chloride. This acid chloride is then condensed with the requisite zinc alkyl iodide, and the mixed *cyclo*acetal obtained is decomposed by alcoholic hydrochloric acid, the ethyl α-hydroxy*iso*butyrate and the ethyl ester of the α-ketonic acid being separated by fractional distillation. The ester is best hydro-

lysed by boiling with aqueous oxalic acid. The following example is given.

Ethyl oxalyl chloride when condensed with α-hydroxy*iso*butyric acid yields *ethyloxalyloxy*iso*butyric acid*, $OEt\cdot CO\cdot CO_2\cdot CMe_2\cdot CO_2H$, m. p. 83°, which gives a *chloride*, b. p. 120·5°/12 mm., and an *anilide*, m. p. 95°. The acid chloride when condensed with zinc propyl iodide yields the cyclo*acetal*, $\begin{array}{l} OEt\cdot CO\cdot CPr\cdot O\cdot CO \\ \qquad\quad\ \ | \qquad\quad\ | \\ \qquad\quad\ O\text{———}CMe_2 \end{array}$ b. p. 123—124°/11 mm., which when boiled with 5% alcoholic hydrochloric acid gives ethyl butyrylformate, $C_3H_7\cdot CO\cdot CO_2Et$, b. p. 71—74°/12 mm. (compare Locquin, *loc. cit.*), together with ethyl α-hydroxy*iso*butyrate and some *diethylacetal* of ethyl butyrylformate, b. p. 96°/41 mm., which can also be prepared by the action of ethyl orthoformate on ethyl butyrylformate, and on hydrolysis with aqueous oxalic acid gives butyrylformic acid in the same way as ethyl butyrylformate. Ethyl butyrylformate, when isolated, has b. p. 70·5°/11 mm., and gives a *phenylhydrazone*, m. p. 80—81°. Butyrylformic acid, obtained by hydrolysis of its ester, has b. p. 79°/12 mm. (compare Moritz, T., 1881, **39**, 17), and gives a phenylhydrazone, m. p. 101—102° (Locquin, *loc. cit.*, gives 98°), a p-*nitrophenylhydrazone*, brown needles, m. p. 205°, and a *semicarbazone*, m. p. 220°. When boiled in alcoholic solution for half an hour with benzaldehyde and β-naphthylamine, butyrylformic acid yields *α-phenyl-β-ethylnaphthacinchonic acid*,



W. G.

Preparation of Formaldehyde from Methane. VEREIN FÜR CHEMISCHE INDUSTRIE IN MAINZ (D.R.-P., 286731; from *J. Soc. Chem. Ind.*, 1916, **35**, 73).—Methane is oxidised to formaldehyde when it is passed, mixed with a large excess of air or oxygen, over a metal or metallic couple at 150—220°. Thus 3 parts of methane and 100 parts of moist air, when passed over copper or silver or both at 150—200°, is partly converted into formaldehyde, and by means of a circulatory system the aldehyde is washed out with water, and the unchanged methane, mixed with more oxygen, returned to the catalyst. G. F. M.

The Characterisation of Chloroketones. E. E. BLAISE (*Bull. Soc. chim.*, 1915, [iv], **17**, 425—428).—The chloro-ketones are best characterised by preparing their semicarbazones under suitable conditions. Owing to the unstable nature of these compounds, their melting points are not always sharp unless taken on a mercury-bath. The semicarbazones are best prepared by adding to the chloro-ketone semicarbazide hydrochloride (1—1·5 mols.) in aqueous solution, filtering, washing the precipitate with water and benzene or chloroform, and, without drying, crystallising the semi-

carbazone from warm benzene. The semicarbazones of the α-chloro-ketones with aqueous potassium carbonate readily yield the semicarbazones of the corresponding keto-alcohols, and with an alcoholic solution of sodium acetate give the acetates of the latter semicarbazones. Under the above conditions, the dichloro-ketones of the type $CHCl_2 \cdot CO \cdot R$ give normal semicarbazones, but with an excess of semicarbazide hydrochloride they yield disemicarbazones of the type $CH(CH_3ON_3) \cdot C(CH_3ON_3)R$, whereas the dichloro-ketones of the type $R \cdot CCl_2 \cdot CO \cdot R'$ always give the disemicarbazones, $R \cdot C(CH_3ON_3) \cdot C(CH_3ON_3)R'$. These disemicarbazones are insoluble in all organic solvents except formic and acetic acids.

Methyl chloroethyl ketone gives a *semicarbazone*,

$$C_2H_4Cl \cdot CMe \colon CH_3ON_3,$$

micaceous plates, m. p. 143—145°, which is converted by aqueous potassium carbonate into the semicarbazone,

$$OH \cdot C_2H_4 \cdot CMe \colon CH_3ON_3,$$

m. p. 202° (compare Kling, A., 1905, i, 172), and with alcoholic sodium acetate gives the *semicarbazone*,

$$CH_3 \cdot CO_2 \cdot C_2H_4 \cdot CMe \colon CH_3ON_3,$$

m. p. 161°.

Dichloromethyl ethyl ketone with 1 mol. of semicarbazide hydrochloride gives the *semicarbazone*, $CHCl_2 \cdot CEt \colon CH_3ON_3$, m. p. 142°, and with 3 mols. of semicarbazide in aqueous alcoholic solution gives *ethylglyoxaldisemicarbazone*,

$$CH(CH_3ON_3) \cdot CEt \colon CH_3ON_3,$$

plates, m. p. above 230°.

Methyl $\alpha\alpha$-dichloroethyl ketone gives with free semicarbazide or its hydrochloride only *diacetyldisemicarbazone*, $[CMe(CH_3ON_3) \cdot]_2$, a sandy, crystalline precipitate, m. p. above 230°.

Chloromethyl α-chloroethyl ketone gives a *semicarbazone*, $CH_2Cl \cdot C(CH_3ON_3) \cdot CHClMe$, m. p. 114°. W. G.

Ammonia Derivatives of the Sugars. P. A. Levene (*J. Biol. Chem.*, 1916, **24**, 59—62).—It has been recently suggested that the so-called glucosimines are in reality not imino-compounds at all, and that from a structural point of view a more correct term would be aminoglucosides (Irvine, Thomson, and Garrett, T., 1913, **103**, 238). An examination of glucosimine, galactosimine, xylosimine, and lyxosimine was made by comparing the nitrogen values obtained by the Kjeldahl process and by the van Slyke method with nitrous acid (A., 1912, ii, 1008). The results indicate the presence of a primary amino-group in the molecule, and thus confirm the view of Irvine, Thomson, and Garrett. Of the four compounds named, lyxosimine was found to be most stable and glucosimine least stable. D. F. T.

The Biochemical Synthesis of Alkyl Glucosides. III. Monoglucosides of Polyhydric Alcohols. Em. Bourquelot (*Ann. Chim.*, 1915, [ix], **4**, 310—379).—A more detailed account of work already published (compare A., 1903, i, 544; 1913, i, 323, 428, 663, 747, 781, 989, 1080, 1305; 1914, i, 499, 662, 1080; 1915, i, 76, 382, 674, 703, 829, 940, 1076). W. G

Modification of Starch by Gaseous Hydrogen Chloride. FRANCIS C. FRARY and ARTHUR C. DENNIS (*J. Ind. Eng. Chem.*, 1915, **7**, 214—216).—Results of experiments in which dry starch was treated with gaseous hydrogen chloride at temperatures varying from 20° to 100° showed that for a given acidity there is a definite temperature range within which heating for thirty minutes will convert the starch into the soluble variety; at higher temperatures the starch is rapidly converted into dextrin. Similarly, for a given temperature, the range of acidity within which a soluble starch is produced in definite, larger quantities of acid producing dextrin, whilst smaller quantities fail to produce the soluble starch. The reaction does not, however, proceed in two stages; dextrin begins to be formed in small quantity as soon as the formation of soluble starch commences. A good white dextrin could be prepared by treating starch with gaseous hydrochloric acid at 100° (the residual acid in the product would have to be neutralised), but the method is not well adapted to the production of soluble starch. W. P. S.

Saccharification of Starch by Hydrofluoric Acid. EDUARD KUNZ (*Chem. Zentr.*, 1915, ii, 783; from *Zeitsch. Spiritusind.*, 1915, **38**, 295—296. Compare Deussen, A., 1905, ii, 311).—The hydrolysing action of hydrofluoric acid on starch is only one-seventeenth as great as that of hydrochloric acid. When the starch is boiled with the more dilute solutions of the acid, the attainment of a high degree of saccharification requires a disproportionately long time. The action of the pure acid is considerably weaker than that of the commercial acid, this being attributed to the presence in the latter of sulphuric and hydrofluosilicic acids, comparatively small admixtures of such acids causing marked increases in the saccharifying power. At higher pressures (and temperatures) the time of saccharification is curtailed, but the decomposition of the sugar is likewise facilitated. Increase in the proportion of the acid leads to rapidly increasing decomposition and reversion of the dextrose. T. H. P.

Ethylaminochromi-compounds. HJ. MANDAL (*Ber.*, 1915, **48**, 2055—2057).—Among the co-ordinated cobalt and chromium compounds there are not many which contain primary aliphatic amines. Such are Tschugaev's compounds,

$$\left[Co(NH_2Et)_2\begin{pmatrix}R\cdot CNO\\ |\\ R\cdot CNO\end{pmatrix}_2H_2\right]X,$$

(A., 1906, i, 814), and the products obtained by Lang with Carson and Joliffe (1903—1904) by the action of methylamine and ethylamine on chromium chloride.

The author has now prepared some chromium salts of the chloropurpureo-series. Thus, by the interaction of anhydrous ethylamine and chromium chloride at below 0°, he has obtained *chloropentaethylaminochromichloride*, $[CrCl(NH_2Et)_5]Cl_2$, a red compound which gives characteristic precipitates with a number of reagents. J. C. W.

Aminoglucoheptonic Acid. P. A. LEVENE (*J. Biol. Chem.*, 1916, **24**, 55—57).—For the purpose of an investigation having as its aim the determination of the configuration of the amino-derivatives of the sugars, for example, glucosamine, aminoglucoheptonic acid was required. This substance, of which an amorphous copper salt has already been described (Neuberg, A., 1903, i, 74; Neuberg and Wolff, A., 1903, i, 319), was prepared by the interaction of glucosamine hydrochloride, hydrocyanic acid, and ammonia in aqueous solution, and was obtained in needles, m. p. 169° (corr.).

D. F. T.

Dibutyramide and Dipropyltriazole with its Salts. W MILLER (*Monatsh.*, 1915, **36**, 929—939).—The author has extended to butyric anhydride the process by which acetic anhydride has recently been made to yield diacetamide (Brunner, A., 1915, i, 1007), but finds that for the production of a good yield of dibutyramide certain modifications are necessary.

When potassium cyanate is gradually added to butyric anhydride at 120°, interaction ceases to occur before the theoretical quantity has been introduced; as soon as this stage is reached it is necessary to cool and to remove the crystallised dibutyramide, when the butyric anhydride mother liquor can again be heated and treated with more cyanate. In this way, most of the anhydride can be finally converted into the secondary amide.

Dibutyramide, $NH(C_4H_7O)_2$, prepared in this way forms a crystalline solid, m. p. 108°, and separates from benzene (probably with benzene of crystallisation) in needles, m. p. near 80°. By heating with semicarbazide hydrochloride and calcium butyrate at 130°, it is converted into hydrazoformamide and dipropyltriazole, together with a small quantity of a crystalline, nitrogenous *compound*, m. p. 155°. The dipropyltriazole, purified by fractional distillation and recrystallisation, was obtained as hygroscopic leaflets, m. p. 67·5°; the *silver* and *mercuric* derivatives were obtained as crystalline solids; *hydrochloride*, apparently octahedral crystals, m. p. 133°. D. F. T.

Preparation of Carbamide. BADISCHE ANILIN & SODA FABRIK. (Eng. Pat., 1914, 24042; from *J. Soc. Chem. Ind.*, 1916, **35**, 71—72).—The formation of carbamide from ammonium carbamate is accelerated by the addition of neutral, acidic, basic, or saline catalysts, such as water (set free from ammonium carbonate), charcoal, sugar, gum, thiocarbamide, carbamide itself, oxides, and salts of alkali or alkaline earth metals, and various acids, either free or as ammonium salts. Thus ammonium carbamate (from solid carbon dioxide and liquid ammonia) mixed with 10—20% of normal ammonium carbonate and heated at 135—140° in closed vessels yields carbamide more quickly than when heated alone, and with better yield than from ammonium carbonate alone.

G. F. M.

A New Series of Platinum Compounds Analogous to Cossa's Salts. L. TSCHUGAEV and W. LEBEDINSKI (*Compt. rend.*, 1916, **162**, 43—45).—By the action of acetonitrile on potassium platinochloride Hofmann and Bugge (A., 1907, i, 489) obtained platinous chloride bisacetonitrile, $PtCl_2,2CH_3\cdot CN$. From the mother liquors of this reaction the authors have isolated another substance. To the aqueous filtrate the chloride of Reiset's base I was added, and the precipitate treated with warm water containing a few drops of hydrochloric acid. A yellow solution was obtained from which Magnus's salt separated, and from the filtrate, on cooling, the *compound*, $(Pt4NH_3)[PtCl_3(CH_3\cdot CN)]_2$, was deposited in quadratic plates. This, when warmed with an excess of hydrochloric acid, was decomposed, giving Magnus's green salt, $(Pt4NH_3)PtCl_4$, chloroplatinous acid, and acetonitrile, which was in turn hydrolysed. In aqueous solution with a solution of potassium platinochloride in the presence of a little hydrochloric acid, the compound gave a *potassium* salt, $K[PtCl_3(CH_3\cdot CN)]$, from which the original compound was regenerated by the addition of the chloride of Reiset's base I. When warmed with hydrochloric acid, the potassium salt was decomposed, forming potassium platinochloride, and with acetonitrile in neutral solution it yielded platinous chloride bisacetonitrile.

From these experiments it follows that acetonitrile behaves in a manner analogous to ammonia and organic amines towards platinochlorides. W. G.

Hydrolytic Products of Bimolecular *iso*Valeryl Cyanide and a New Preparation of *iso*Butyltartronic Acid. JOSEF PLATTNER (*Monatsh.*, 1915, **36**, 899—910).—Three methods of preparation have hitherto been applied to the bimolecular acyl cyanides, namely, the polymerisation of the simple acyl cyanides, especially under the influence of solid alkali hydroxide or of sodium, the action of the acid anhydrides on potassium cyanide, and the action of acyl chlorides on hydrogen cyanide in ethereal solution in the presence of pyridine. By one or other of these methods the bimolecular cyanides derived from the acetyl, propionyl, and the two butyryl radicles have been obtained, and the author has now extended the knowledge in this field by the preparation and examination of derivatives of bimolecular *iso*valeryl cyanide.

Bimolecular iso*valeryl cyanide* was obtained by the interaction of *iso*valeric anhydride and potassium cyanide in the cold, but the product was an oil, and could not be freed from admixed anhydride and acid. On treatment of the cyanide with hot hydrochloric acid there was liberation of carbon dioxide, and hydrolysis was therefore effected by treating in the cold with the calculated quantity of water mixed with sulphuric acid (1 : 7 by weight); in this way there was obtained, together with the corresponding unimolecular amide, the bimolecular, iso*valerylformamide*,

$$CHMe_2\cdot CH_2\cdot C(CO\cdot NH_2)_2\cdot O\cdot CO\cdot CH_2\cdot CHMe_2,$$

lustrous leaflets, m. p. 167°, which was further hydrolysed by boil-

ing dilute hydrochloric acid to *iso*butyltartronic acid,

$$CHMe_2\cdot CH_2\cdot C(CO_2H)_2\cdot OH,$$

deliquescent, microscopic tablets, m. p. 107° with decomp. (compare Guthzeit, A., 1882, 239); the *lead*, *silver*, *barium*, and *phenylhydrazine* salts were obtained as crystalline solids, the last having m. p. 136° (decomp.).

iso*Valerylformamide* (*a-keto-γ-methylvaleramide*),

$$CHMe_2\cdot CH_2\cdot CO\cdot CO\cdot NH_2,$$

obtained in the preparation of the bimolecular compound, and produced in better yield by using for the hydrolysis of the dicyanide a cold mixture of sulphuric acid and water in the proportions 70 : 5, forms large tablets, m. p. 60°. This substance on hydrolysis with warm dilute hydrochloric acid gave *a-keto-γ-methyl*-n-*valeric acid*, an uncrystallisable syrup which was analysed as the *silver* salt, a yellowish-white, granular, crystalline powder, and as the *phenylhydrazone*, yellow, silky needles. D. F. T.

Syntheses of Hydrocarbons in the Aryl and *cyclo*Hexane Series. PAUL SABATIER and MARCEL MURAT (*Ann. Chim.*, 1915, [ix], **4**, 253—309).—A résumé of work already published (compare A., 1903, i, 393, 453, 454, 733; 1905, i, 254, 267, 333, 401, 587; 1907, i, 587, 747; 1910, i, 668, 669; 1912, i, 353, 414, 547, 617, 757; 1913, i, 255, 330, 362, 468, 700, 716, 845; 1914, i, 168, 323, 400, 404, 547, 548, 1068; ii, 276, 729). W. G.

Aromatic Nitro-derivatives. V. Reactivity of the Nitro-group in Aromatic Compounds. MICHELE GIUA (*Gazzetta*, 1915, **45**, ii, 348—362. Compare A., 1915, i, 659).—The *compound*, $\begin{matrix}H\\OH\end{matrix}\!>C<\!\begin{matrix}C(NO_2):CH\\C(NO_2):CH\end{matrix}\!>C:NO\cdot ONa$, prepared by the action of sodium hydroxide on *s*-trinitrobenzene in acetone solution, forms reddish-brown crystals exploding when heated, and yields the original trinitrobenzene when treated with acid.

The following further systems have been analysed thermally. With *m*-dinitrobenzene–diphenylamine, 2 : 4-dinitrotoluene–diphenylamine, and 2 : 4 : 6-trinitrotoluene–diphenylamine, compounds are formed which dissociate in the fused state, but in no case is any indication obtained of the formation of a compound with a definite melting point. The system *m*-dinitrobenzene–acenaphthene forms a compound, m. p. 72·3°, containing 50 mols. % of each component and two eutectics. 2 : 4-Dinitrotoluene–acenaphthene yields a similar compound, m. p. 61° (compare Buguet, A., 1910, i, 105). 2 : 4 : 6-Trinitrotoluene–acenaphthene yields a compound, m. p. 109·7°, which may be obtained in shining, yellow needles by crystallising a fused mixture of the components in molecular proportions from alcohol (compare Buguet, *loc. cit.*).

To the saline products of nitro-derivatives which were described by Hantzsch, and do not give the original nitro-derivatives when treated with an acid, constitutional formulæ such as those of Angeli (A., 1898, ii, 216) or Meisenheimer (A., 1902, i, 795) can scarcely be attributed. In these cases the nitrogen of the nitro-

group also exerts a function, and becomes less strongly linked to the carbon atom of the aromatic nucleus, a less stable complex resulting; it is, indeed, found that all these substances explode more or less readily when heated. With sodium ethoxide, *m*-dinitrobenzene forms only the compound $C_6H_4(NO_2)_2$,NaOEt; 2:4-dinitrotoluene gives the compounds $C_6H_3Me(NO_2)_2$,NaOH and $C_6H_3Me(NO_2)_2$,2NaOEt,EtOH, and 2:4:6-trinitrotoluene the compound $C_6H_2Me(NO_2)_3$,NaOEt. T. H. P.

An Anisotropic Aqueous Solution. HÅKAN SANDQVIST (*Ber.*, 1915, **48**, 2054—2055).—For every concentration there is a definite point at which solutions of 10-bromophenanthrene-3(or 6)-sulphonic acid (A., 1913, i, 846) become clear or turbid, as the case may be. Thus, a 0·5*N*-solution shows a sharp transition at 22·83°, a 0·319*N*-solution at 9·47°. The agreement between the points at which the solutions become clear or turbid shows that the turbid phase is not a supersaturated solution. The microscope reveals it to be rather a "liquid crystal." J. C. W.

The Resolution of Asymmetric Quinquevalent Nitrogen Compounds. JOSEPH REILLY (*Proc. Camb. Phil. Soc.*, 1915, **18**, 177).—Weak acids like tartaric or camphoric sometimes effect the resolution of quinquevalent nitrogen derivatives when stronger acids, such as β-camphorsulphonic or α-bromocamphor-π-sulphonic, fail, and vice versâ. The active phenylbenzylmethylallylammonium iodide originally obtained by Pope and Peachey (T., 1899, **75**, 1127) was obtained by fractional crystallisation of phenylbenzylmethylallyl *d*- or *l*-β-camphorsulphonate, and subsequent decomposition of the resulting product with potassium iodide. The resolution is much more difficult if α-bromocamphor-π-sulphonate is used. It has been suggested that this selective action may be due to racemisation or to hydrolytic dissociation of the salts, but the author considers that similar solubilities of the *d*B*d*A and *l*B*d*A compounds is a more likely explanation. By the action of anhydrous silver *d*- and *l*-α-bromocamphor-π-sulphonates and *d*- and *l*-phenylbenzylmethylallylammonium iodides under different conditions, the compounds *d*B*d*A, *d*B*l*A, *l*B*l*A, and *l*B*d*A were obtained. These compounds are of the same order of stability as the corresponding β-camphorsulphonates, and show only a very slight tendency to racemise at the ordinary temperature in water. The first-mentioned compound can be recrystallised from dry ethyl acetate without change of activity, but on recrystallisation from alcohol a slight fall, and on crystallisation from chloroform a greater fall in rotation was observed.

T. S. PA.

Preparation of Diaminodiphenylcarbamidetetrasulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 286752; from *J. Soc. Chem. Ind.*, 1916, **35**, 36).—A diaminodiphenylcarbamidetetrasulphonic acid in which the sulphonic groups are in the meta-position to the carbamide residue is obtained

by the action of carbonyl chloride on *p*-phenylenediaminedisulphonic acid in presence of a substance capable of combining with an acid. In the azo-dyes derived from this acid the sulphonic groups will occupy the ortho-position to the azo-group, in which position they exert a favourable influence on the affinity of the dye for cotton and its fastness to light. G. F. M.

Action of Derivatives of Phenols on Ethyl Diazoacetate. II. G. CALCAGNI (*Gazzetta*, 1915, **45**, ii, 362—368).—By the method previously employed (A., 1915, ii, 14), the author has investigated at the ordinary temperature the hydrogen-ion concentration of saturated aqueous solutions of *o*-, *m*-, and *p*-nitrophenols, α- and β-naphthols, tribromo- and trichloro-phenols, rosolic acid, phenolphthalein, alizarin and helianthin, and of an $N/10$-solution of *p*-chlorophenol and an $N/20$-solution of picric acid; the water used had the conductivity $1\cdot5\times10^{-6}$. In some cases, constant conductivity could not be attained, and in others the values found are extremely small, owing to the very slight solubilities. For those of the compounds with which satisfactory results were obtained the results are as follows: *p*-chlorophenol, $K=0\cdot0001072$, $C_H=0\cdot0_52784$; picric acid, $K=0\cdot2061$, $C_H=0\cdot005353$; *o*-nitrophenol, $K=0\cdot0005485$, $C_H=0\cdot0_41425$; *p*-nitrophenol, $K=0\cdot001230$, $C_H=0\cdot0_43195$; helianthin, $K=0\cdot001226$, $C_H=0\cdot0_43184$. The values of C_H given are not very accurate, owing to the lack of strict proportionality between K and C_H. The specific conductivities at 25° are: picric acid, 0·003631; *p*-chlorophenol, $0\cdot0_52341$; *o*-nitrophenol, $0\cdot0_54960$; *p*-nitrophenol, $0\cdot0_41373$; helianthin, $0\cdot0_41923$; α-naphthol, $0\cdot0_5327$; β-naphthol, $0\cdot0_52336$; trichlorophenol, $0\cdot0_55215$; tribromophenol, $0\cdot0_53252$; alizarin, $0\cdot0_51992$. In the case of derivatives of phenol, the acidity depends on the nature and number of the groups introduced into the molecule.

T. H. P.

ββ-Dinaphthol and 2-Hydroxy-α-naphthyl β-Naphthyl Ether. O. HINSBERG (*Ber.*, 1915, **48**, 2092—2095. Compare A., 1915, i, 810).—A reduction product, m. p. 197°, was recently obtained from dehydro-β-naphtholsulphone which was supposed to be a ββ-dinaphthol. It is now found that it gives only mono-acyl derivatives, and from its mode of formation and properties it is regarded as *2-hydroxy-α-naphthyl β-naphthyl ether*, $OH\cdot C_{10}H_6\cdot O\cdot C_{10}H_7$. The *acetate* has m. p. 115°, and retains solvent acetic acid somewhat firmly, whence it was originally regarded as a diacetate. The m-*nitrobenzenesulphonate*, $C_{20}H_{13}O\cdot O\cdot SO_2\cdot C_6H_4\cdot NO_2$, forms colourless clusters of needles, m. p. 139°, and the p-*nitrobenzoate* crystallises in pale yellow rosettes, m. p. 154°.

An attempt was made to synthesise the compound by condensing 1-bromo-β-naphthol with β-naphthol in the presence of a solution of sodium in dilute methyl alcohol, but the product of the reaction was ββ-dinaphthol, m. p. 216°. This dinaphthol was also prepared by heating 1-bromo-β-naphthol with copper powder at 230°.

J. C. W.

Preparation of Aromatic Tellurium Compounds. KARL LEDERER (*Ber.*, 1915, **48**, 2049—2054. Compare A., 1915, i, 1056). —Further examples of the preparation of tellurides and ditellurides by the action of tellurium dihaloids on magnesium aryl haloids. The *p*-anisyl and *p*-phenetyl tellurides obtained in this way differ from those obtained by Rohrbaech (A., 1901, i, 273) by reducing the products of the action of tellurium tetrachloride on the two ethers (Rust, A., 1898, i, 137) with zinc. It is believed that the earlier compounds are not para-substituted tellurides, but methylene compounds, thus:

$$2C_6H_5\cdot OMe + TeCl_4 \longrightarrow TeCl_2(CH_2\cdot OPh)_2 \text{ (Rust)};$$
$$\longrightarrow Te(CH_2\cdot OPh)_2 \text{ (Rohrbaech)}.$$

Magnesium *p*-tolyl bromide reacted with tellurium dibromide or di-iodide to give a little di-*p*-tolyl, some resinous di-*p*-tolyl ditelluride, and chiefly di-*p*-tolyl telluride, which was purified by conversion into the dibromide, and reducing this by sodium sulphite. It had m. p. 69—70° and b. p. 211—212°/18 mm. (compare Zeiser, A., 1895, i, 512). Magnesium *o*-tolyl bromide was also treated with tellurium dichloride or dibromide, and di-*o*-tolyl telluride was obtained with m. p. 37—38°, b. p. 202—203°/15 mm. (*ibid.*).

Anisole and phenetole were heated with tellurium tetrachloride until solid products were obtained, and these were reduced to tellurides by means of sodium hyposulphite. The telluride from anisole formed dark red needles, m. p. 50°; the phenetole compound orange-red leaflets, m. p. 64°. The anisole derivative was warmed with methyl iodide, and the product was converted into a picrate, which seems to be *anisyldimethyltelluronium picrate*, $TeMe_2\cdot C_7H_7O,C_6H_3O(NO_2)_3$, yellow crystals, m. p. 126—127°. The elimination of one anisyl residue on methylation is evidence in favour of the assumption that the tellurium is attached to the alkyl group in these tellurides. J. C. W.

Isomerisation of *cyclo*Pentylcarbinol on Conversion into Halogen Derivatives. S. S. NAMETKIN and (MLLE.) O. N. MOROZOVA (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1607—1610).—It has been previously shown (A., 1912, i, 172) that the action of fuming hydriodic acid on *cyclo*pentylcarbinol, and reduction of the resulting iodo-derivative by means of zinc dust in aqueous alcohol, yields a product containing *cyclo*hexane. Further experiments on this question have now been carried out in the following manner. *cyclo*Pentylcarbinol was converted in various ways into the corresponding haloid derivatives, which, after distillation under diminished pressure, were converted by the Grignard reaction into the organo-magnesium compound, the latter being then transformed by the action of oxygen, etc., into the alcohol. The properties of this alcohol and of its urethane were compared with those of the original alcohol, and the formation of adipic acid by oxidation of the final alcohol with nitric acid was also investigated.

The results show that, in aqueous solution, hydrochloric, hydrobromic, or hydriodic acid causes partial isomerisation of the five-

membered ring-system of *cyclo*pentylcarbinol into a six-membered one at 100—105°. The extent of the isomerisation is in all cases of the order of 50%, and appears to depend but little on the nature of the halogen hydracid. Less marked, but undoubted, isomerisation takes place when the *cyclo*pentylcarbinol is treated with iodine and red phosphorus. Since such a stable alicyclic system as that of *cyclo*pentane is so easily isomerised under the influence of halogen hydracids, the question arises whether the same may not occur under similar conditions with the analogous *cyclo*hexane.

T. H. P.

Production of *o*-Sulphamidobenzoyl-*p*-phenetidine. CHEMISCHE FABRIK VORM. SANDOZ (Eng. Pat., 1915, 9511; from *J. Soc. Chem. Ind.*, 1916, **35**, 72).—*o*-Sulphamidobenzoyl-*p*-phenetidine is obtained as a crystalline powder by heating *p*-phenetidine with *o*-benzoylsulphimide or with methyl or ethyl *o*-sulphamidobenzoate for some hours at 120° out of contact with air, and, after boiling with water, treating with sodium carbonate to slight alkalinity. It is non-poisonous, has antipyretic and hypnotic properties, and although comparatively easily saponified by dilute alkalis, is resistant to dilute acids.

G. F. M.

The Action of Sunlight on the Cinnamic Acids. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 751—756).—The author finds that the methods described by Erlenmeyer and Barkow (A., 1906, i, 429) for the preparation of α- and β-storax-cinnamic acids are not entirely satisfactory, and, indeed, the method for the conversion of the α-acid into the β-isomeride by heating above the m. p. of the former is stated not to achieve the desired result. According to the author's experience, the β-acid is most conveniently obtained by pouring an alcoholic solution of the α-isomeride, saturated at the ordinary temperature, into a large quantity of water. It may also be obtained by allowing warm solutions of cinnamic acid to crystallise, the lower the temperature of crystallisation the more favourable being the conditions for the formation of the β-acid. Experiments on the spontaneous change of the β-acid into the α-isomeride indicate that both at the ordinary temperature and also at higher temperatures the former acid is metastable.

On the assumption that in the solid condition these acids exist in a bimolecular condition, the author suggests the structures $O{<}\begin{matrix}CHPh\cdot CH_2\cdot CO\\CO\cdot CH_2\cdot CHPh\end{matrix}{>}O$ and

$$CHPh{:}CH\cdot C(OH){<}\begin{matrix}O\\O\end{matrix}{>}C(OH)\cdot CH{:}CHPh$$

for the α- and β-acids respectively. This view receives confirmation from the fact that the solid potassium, calcium, and barium salts of either the α- or the β-acid, when exposed to light, yield only β-truxillic acid, which result indicates that only the β-isomeride is capable of forming salts.

D. F. T.

The Nitration of Phenylpropiolic Acid. S. REICH (*Compt. rend.*, 1916, **162**, 129—130).—Phenylpropiolic acid can be nitrated without the side-chain being oxidised if the acid is added in small portions to nitric acid (D 1·50) at $-20°$. The product of the nitration is *p*-nitrophenylpropiolic acid. If the nitration is effected at 0°, a small amount of *o*-nitrophenylpropiolic acid is also obtained. In neither case could any *m*-nitrophenylpropiolic acid be detected. The group $\cdot C\vdots C\cdot CO_2H$ thus orientates the $\cdot NO_2$ group into the para-, and secondarily into the ortho-position. In this respect phenylpropiolic acid resembles cinnamic and phenylpropionic acids in its behaviour. W. G.

Abietic Acid. PETER POOTH (*Chem. Zentr.*, 1915, ii, 790; from *Farbenzeit.*, 1915, **20**, 1056—1059).—A critical discussion of publications dealing with the constitution of abietic acid.
T. H. P.

Phenyl Propyl Ketone. E. GRAZIANO (*Gazzetta*, 1915, **47**, 390—396).—Phenyl propyl ketone (compare Senderens, A., 1910, i, 179) forms colourless crystals, m. p. 11°, b. p. 231°/727 mm., D_4^{15} 0·992, and yields a highly fluorescent solution with concentrated sulphuric acid. Its o-*tolylhydrazone*,

$$CPhPr\colon N\cdot NH\cdot C_6H_4Me,$$

is an oil, and its p-*tolylhydrazone* forms colourless or faintly yellow needles, m. p. 72°. The s-ψ-*cumylhydrazone*,

$$CPhPr\colon N\cdot NH\cdot C_6H_2Me_3,$$

forms colourless or faintly yellow needles, m. p. 105°. The as.-m-*xylylhydrazone*, $CPhPr\colon N\cdot NH\cdot C_6H_3Me_2$, forms colourless or pale yellow needles, and, like the two preceding compounds, is moderately stable in alcoholic solution, but unstable in the solid state, determination of the melting point in this case being impossible.

The oxime undergoes the following series of transformations: $CPhPr\colon NOH \longrightarrow CPhPr\colon NCl \longrightarrow CPrCl\colon NPh \longrightarrow OH\cdot CPr\colon NPh \longrightarrow C_3H_7\cdot CO\cdot NHPh \longrightarrow NH_2Ph + C_3H_7\cdot CO_2H$, so that it has the configuration $\begin{array}{c} C_3H_7\cdot C\cdot C_6H_5 \\ \| \\ N\cdot OH \end{array}$

The energetic action of nitric acid on the ketone yields benzoic and propionic acids, but when the action is moderated (compare Fileti and Ponzio, A., 1895, i, 499) the products appear to contain phenyl ethyl diketone and a dinitroso-derivative decomposing violently at 100° with evolution of nitrous vapours. T. H. P.

Stereochemistry of the Quinone-oximes. F. KEHRMANN (*Ber.*, 1915, **48**, 2021—2035).—An account of some orienting work on the quinone-oximes, completed in 1902 in extension of earlier work (A., 1900, i, 180).

VII. *Monoximes of the* 3-*Halogeno*-2:5-*toluquinones*. [With F. MUSSMANN and CARLO FACCHINETTI.]—The preparation and reactions of 3-iodo-2:5-toluquinone monoxime have already been

described (A., 1889, 993), and an account of the chloro- and bromo-compounds is now given.

3-Chloro-2 : 5-toluquinone, prepared by oxidising dichloro-*o*-cresol with chromic and acetic acids, was converted into 3-*chloro*-2 : 5-*toluquinone*-5-*oxime*, $O:C_7H_5Cl:N\cdot OH$, which crystallised in glistening, pale yellow leaflets, and yielded an *acetyl* derivative, $C_9H_8O_3NCl$, which crystallised in two forms, namely, pale yellow, stable needles, m. p. 72°, and stout, amber-coloured prisms, m. p. 62°. The oxime was reduced by means of stannous chloride to 3-*chloro*-5-*amino*-o-*cresol*, colourless needles, m. p. 137°, which quickly darkened in the air, and also oxidised by means of cold dilute nitric acid to 3-*chloro*-5-*nitro*-o-*cresol*, pale yellow prisms, m. p. 122°.

3-*Bromo*-2 : 5-*toluquinone* was obtained from dibromo-*o*-cresol in long, orange-yellow needles, m. p. 93·5°, and converted into 3-*bromo*-2 : 5-*toluquinone*-5-*oxime*, $C_9H_8O_3NBr$, which crystallised in lemon-yellow leaflets, and yielded two *acetyl* derivatives, the stable one having m. p. 74°, the labile one m. p. 71°. The oxime was reduced to 3-*bromo*-5-*amino*-o-*cresol*, needles, m. p. 142° (*hydrochloride*, colourless needles; *acetyl* derivative, needles, m. p. 165°), and oxidised by cold dilute nitric acid to 3-bromo-5-nitro-*o*-cresol, m. p. 120·5°, and by hot dilute nitric acid to 3 : 5-*dinitro*-o-*cresol*, yellow needles, m. p. 85·5°.

VIII. *Dioxime of* 4-*Chloro*-2 : 5-*toluquinone and the Monoximes of* 4 : 6- *and* 3 : 6-*Dichloro*-2 : 5-*toluquinones*. [With GIUSEPPE SILVA and CORNELIUS KELETI.]—Both modifications of 4-chloro-2 : 5-toluquinonemonoxime (A., 1899, i, 128) yielded the *dioxime*, $C_7H_7O_2N_2Cl$, when boiled with an excess of hydroxylamine hydrochloride in concentrated alcoholic solution, with the occasional addition of sodium carbonate. The dioxime was obtained as a microcrystalline powder, decomp. about 240°, which formed a sodium salt, in stout, golden-yellow prisms, and yielded only one *diacetyl* derivative, $C_{11}H_{11}O_4N_2Cl$, in stout prisms, decomp. about 185°. It was reduced to 4-chlorotolylene-2 : 4-diamine, which was characterised by the *hydrochloride*, $CH_3\cdot C_6H_2Cl(NH_2)_2,2HCl$, and the *diacetyl* compound, silky, snow-white needles. The dioxime was also oxidised by means of an alkaline solution of potassium ferricyanide to 4-*chloro*-2 : 5-*dinitrosotoluene*, a lemon-yellow powder, decomp. 163—165°, and this was oxidised by warm concentrated nitric acid to 4-*chloro*-2 : 5-*dinitrotoluene*, which crystallised in stout, amber-yellow prisms, m. p. 107°.

4-Chloro-2 : 5-toluquinone was treated with fuming hydrochloric acid, when it yielded a mixture of di- and tri-chloroquinols. This was oxidised, and 4 : 6-*dichloro*-2 : 5-*toluquinone* was isolated from the product in golden-yellow leaflets, m. p. 85—86°, which yielded 4 : 6-*dichloro*-2 : 5-*toluquinone*-2-*oxime*, $O:C_7H_4Cl_2:N\cdot OH$, pale yellow needles. The oxime formed a *benzoyl* derivative, m. p. 154°, was oxidised by dilute nitric acid to 2 : 4-*dichloro*-6-*nitro*-m-*cresol*, long, pale yellow, glistening needles, m. p. 128°, and converted by means of stannous chloride into 4 : 6-dichlorotoluquinol.

3-Chloro-2 : 5-toluquinone was converted, as above, into 3 : 6-

dichloro-2 : 5-*toluquinone*, leaflets, m. p. 76°, with alcohol of crystallisation in long, golden prisms, m. p. 67°, and this yielded the corresponding *quinol*, $C_7H_6O_2Cl_2$, needles, m. p. 85°, which formed a *diacetate*, m. p. 110·5°. The quinone gave rise to 3 : 6-*dichloro*-2 : 5-*toluquinone*-5-*oxime*, pale yellow needles, m. p. 135° (decomp.), and this formed an *acetyl* derivative, $C_9H_7O_3NCl_2$, compact, rhombic, pleochroïc crystals [$a:b:c = 0·86265:1:1·1592$], m. p. 85°. The oxime was also reduced to 3 : 6-*dichloro*-5-*amino*-o-*cresol*, stout needles, m. p. 128° (*diacetyl* derivative, m. p. 129°), and oxidised to 3 : 6-*dichloro*-5-*nitro*-o-*cresol*, pale yellow crystals, m. p. 135° (*acetate*, m. p. 98°). J. C. W.

Acenaphthenequinonearylhydrazones. A. Cruto (*Gazzetta*, 1915, **45**, ii, 329—335).—Acenaphthenequinonephenylmethylhydrazone (compare Auwers, A., 1911, i, 171) may be obtained directly from methyl sulphate and acenaphthenequinonephenylhydrazone, Auwers's view that the latter is a true phenylhydrazone of the formula $C_{10}H_6<\begin{matrix}C:N_2HPh\\|\\CO\end{matrix}$, and not a hydroxyazo-compound of the structure $C_{10}H_6<\begin{matrix}C·N:NPh\\||\\C·OH\end{matrix}$, being thus confirmed. Various other arylhydrazones of acenaphthenequinone have been prepared, their *N*-methyl derivatives, that is, the arylmethylhydrazones, being in some cases obtained by the action of methyl sulphate.

Acenaphthenequinone-o-*tolylhydrazone*,

$$C_{11}H_6O:C:N·NH·C_6H_4Me,$$

forms shining, red needles, m. p. 175°, and dissolves in concentrated sulphuric acid, giving an intense blue coloration. The m-*tolylhydrazone* forms small, shining, yellow prisms, m. p. 134°, and gives a deep red solution in concentrated sulphuric acid. The p-*tolylhydrazone* forms long, orange-red crystals, m. p. 163°, and is only slightly hydrolysed on prolonged boiling with concentrated hydrochloric acid.

The as.-m-*xylylhydrazone*, $C_{11}H_6O:C:N·NH·C_6H_3Me_2$, forms long, ruby-red prisms, m. p. 183°, and gives a reddish-brown solution in concentrated sulphuric acid. The as.-m-*xylylmethylhydrazone*, $C_{11}H_6O:C:N·NMe·C_6H_3Me_2$, forms small, red prisms, m. p. 157°.

The ψ-*cumylhydrazone*, $C_{11}H_6O:C:N·NH·C_6H_2Me_3$, forms long, bright red needles, m. p. 292°, and dissolves in concentrated sulphuric acid with a red coloration.

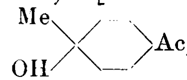
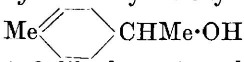
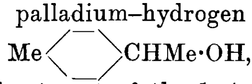
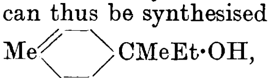
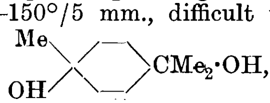
The o-*anisylhydrazone*, $C_{19}H_{14}O_2N_2$, forms dull, deep red prisms, m. p. 218°, and in concentrated sulphuric acid yields an intense blue solution. The p-*anisylhydrazone* forms intense garnet-red needles, m. p. 157°, and in concentrated sulphuric acid gives a brownish-yellow solution showing intense blue fluorescence.

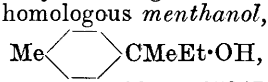
The p-*phenethylhydrazone*, $C_{20}H_{16}O_2N_2$, forms minute, bright red needles, m. p. 151°, and dissolves in concentrated sulphuric acid, giving a yellow solution which shows blue fluorescence.

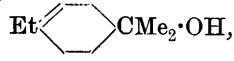
The p-*bromophenylhydrazone*, $C_{18}H_{11}ON_2Br$, forms minute yellow needles, m. p. 193°, and gives an intense ruby-red coloration with

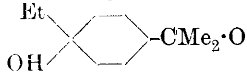
concentrated sulphuric acid. The p-*bromophenylmethylhydrazone*, $C_{19}H_{13}ON_2Br$, forms shining, orange-yellow needles, m. p. 143°.

T. H. P.

Synthesis of Terpineols and Terpins. O. WALLACH [with HANS BERTHOLD, LOUIS AUGSPURGER, HANS WOERLITZER, and FRIEDRICH POHLE] (*Chem. Zentr.*, 1915, ii, 824—829; from *Nachr. K. Ges. Wiss. Göttingen*, 1915, 1—27).—[With HANS BERTHOLD.]—The saturated hydroxy-ketone, , obtained as an intermediate product in the oxidation of β-terpineol to 1:4-methyl*cyclo*hexenyl methyl ketone, is also formed when the latter is hydrated by shaking with 4% sulphuric acid solution for six to eight weeks; it forms a *semicarbazone*, m. p. 197—198°. The *dibromide*, $C_9H_{14}OBr_2$, m. p. 61°, does not lose its bromine when treated with aqueous potassium hydroxide; when boiled with acetic acid, it undergoes marked resinification and yields a little *p*-tolyl methyl ketone. When reduced by means of nascent hydrogen, 1:4-methyl*cyclo*hexenyl methyl ketone yields the lower homologue of terpineol,  (compare A., 1902, i, 803), which gives 1:8-dihydroxy-1-methyl-4-ethyl*cyclo*hexane, $C_9H_{18}O_2$, m. p. 94—95°, when treated with dilute sulphuric acid. Reduction of 1:4-methyl*cyclo*hexenyl methyl ketone with palladium–hydrogen gives 8-*hydroxy*-1-*methyl*-4-*ethyl*cyclo*hexane*, , b. p. 203—205°, D^{17} 0·9110, n_D 1·46405. Treatment of the 1:4-methyl*cyclo*hexenyl methyl ketone obtained from β-terpineol with magnesium methyl iodide leads to the formation of α-terpineol, which can thus be synthesised from the β-modification. *Homo-α-terpineol*, , b. p. 235—237°, D^{20} 0·9390, n_D 1·4850, is similarly prepared by the action of magnesium ethyl iodide. When heated with sodium methoxide, the oily *dibromide*, $C_{11}H_{19}Br_2$·OH, yields a homologous pinol, which passes readily into the higher homologous cymene, 1-methyl-4-*iso*butylbenzene, C_6H_4Me·CHMeEt. Treatment of homo-α-terpineol with permanganate gives a trihydric alcohol, $C_{11}H_{19}(OH)_3$, b. p. 140—150°/5 mm., difficult to purify. The homologous 1:8-*terpin*, , m. p. 65—67°, is obtained by shaking homo-α-terpineol with dilute sulphuric acid. The homologous *menthanol*,

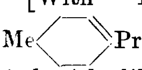


b. p. 106—108°/5 mm., or 223—225°/760 mm., D^{19} 0·9115, n_D 1·4683, formed by reducing homo-α-terpineol with palladium–hydrogen, gives a *phenylurethane*, m. p. 115—120°, and seems to be a mixture. The *homo-α-terpineol*, , m. p.

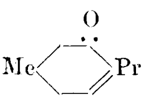
92—94°, b. p. 226—227°, D^{18} 0·943, n_D 1·4811, obtained from ethylnopinol (A., 1908, i, 429), is isomeric with that described above. The corresponding terpin, 1 : 8-*dihydroxy*-1-*ethyl*-4-iso*propyl*cyclo*hexane*, 

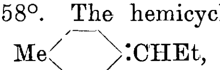
m. p. 75—76° (with water of crystallisation), is obtained by treatment with 5% sulphuric acid solution.

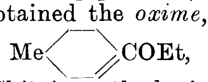
[With Hans Berthold.]—The simple unsaturated alcohols described above were converted into aromatic hydrocarbons by treatment with bromine (1 mol.) in acetic acid and boiling until evolution of hydrogen bromide ceases. In this way, α-terpineol dibromide yields cymene, b. p. 174—175°, D^{20} 0·8575, n_D 1·4909; 7-hydroxy-1-methyl-4-ethyl-Δ^1-*cyclo*hexene gives 1-methyl-4-ethylbenzene; homo-α-terpineol or the homologous pinol (*vide supra*) yields 1-methyl-4-*iso*butylbenzene, and the homo-α-terpineol from ethylnopinol gives 1-ethyl-4-*iso*propylbenzene.

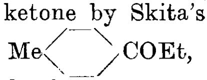
[With Louis Augspurger.]—4-*Methyl*-1-*propyl*cyclo*hexene*, 

prepared by heating 1-methyl-4-propyl*cyclo*hexan-4-ol with dilute sulphuric acid, was not obtained of constant boiling point. The fraction, b. p. 173—176°, yields a *nitrosochloride*, m. p. 134—135°, a *nitrosate*, m. p. 119°, and a *nitrolpiperidide*, m. p. 150—152°. Scission of hydrogen chloride from the nitrosochloride gives the liquid oxime of 4-*methyl*-1-*propyl*cyclo*hexen*-6-*one* (annexed formula), b. p. 220—223° (darkening), 95—98°/12 mm., D^{20} 0·9225, n_D 1·4732; the *semicarbazone*, $C_{11}H_{19}ON_3$, has m. p. 153—154°. Reduction of this ketone yields 1-*methyl*-4-*propyl*cyclo*hexan*-3-*one* (normal menthone), $C_{10}H_{18}O$, b. p. 215—217°, D^{19} 0·8960, n_D 1·4511, which is a colourless liquid having no odour of menthone; its *semicarbazone*, $C_{11}H_{21}ON_3$, m. p. 149—152°, and *oxime*, m. p. 87—88°, were prepared. Oxidation of the ketone by means of chromic acid gives a ketonic acid with the same number of carbon atoms; the *semicarbazone* of the acid, $C_{11}H_{21}O_3N_3$, has m. p. 156—158°. The hemicyclic hydrocarbon,



1-*methyl*-4-*propenyl*cyclo*hexane*, 

b. p. 173—174°, D^{20} 0·8110, n_D 1·4571, which is isomeric with 4-methyl-1-propyl*cyclo*hexene (*vide supra*), is obtained by the method previously given (A., 1908, i, 405) from the condensation product of ethyl α-bromo-*n*-butyrate and 1-methyl*cyclo*hexan-4-one, and yields a *nitrosochloride*, m. p. 138—140°, and a *nitrolpiperidide*, m. p. 148—149°. From the nitrosochloride is obtained the *oxime*, m. p. 105—106°, of the unsaturated *ketone*, 

b. p. 230—231°. Reduction of the ketone by Skita's method gives the saturated extracyclic *ketone*, 

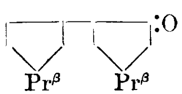
b. p. 210—211°, D^{18} 0·9090, n_D 1·4541, which forms a *semicarbazone*, m. p. 182—183°, and an *oxime*, $C_{10}H_{18}$:NOH, m. p. 95—96°; the specific gravity of the saturated extracyclic ketone is higher than that of

the cyclic ketone. The same normal menthone is obtained by the reduction, according to Skita's method, of i-1-*methyl-4-allyl*cyclo*hexan-3-one*, which is prepared from *i*-1-methyl*cyclo*hexan-3-one, has an odour resembling that of isonitriles, and yields an *oxime*, m. p. 99—100° (not sharp), and a *semicarbazone*, m. p. 125—128° (not sharp).

[With HANS WOERLITZER.]—*α*- and *β*-Tanacetonedicarboxylic acids may be converted into tanacetophorone in the following manner (compare A., 1912, i, 262). Esterification of the ketonic acid by means of alcoholic hydrogen chloride yields an ester hydrochloride, which is transformed into tanacetophorone by sodium alkyloxide. 2-*Methyl*-4-iso*propyl*-$\Delta^{1:3}$-cyclo*pentadiene*,

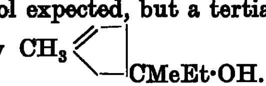
$$CH_2<\begin{matrix}CH{=}CMe\\ CPr^{\beta}{:}CH\end{matrix},$$

obtained by the action of magnesium methyl iodide on tanacetophorone, is a liquid, b. p. 166—167°, D^{21} 0·845, n_D 1·4913, which readily undergoes change in the air. iso*Propyl*cyclo*pentene*iso*propyl*cyclo*pentanone*, $C_{16}H_{26}O$, m. p. 77—78°, prepared by the action of sodium ethoxide on *iso*propyl*cyclo*pentanone, yields an *oxime*, m. p. 125—149°, and a *semicarbazone*, m. p. 192·5°. Reduction of the unsaturated ketone with palladium–hydrogen in methyl alcohol yields iso*propyl*cyclo*pentyl*iso*propyl*cyclo*pentanone* (annexed

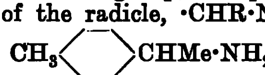


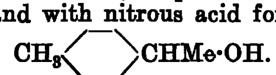
formula), as a colourless, odourless oil, m. p. 157—165°/11 mm., which solidifies in a freezing mixture, and forms an *oxime*, m. p. 136° (decomp. at 120°). Reduction of the saturated or unsaturated ketone with sodium ethoxide gives iso*propyl*cyclo*pentyl*iso*propyl*cyclo*pentanol*, $C_{16}H_{29}{\cdot}OH$, b. p. 160—164°/11 mm., which solidifies in the cold, and forms a *phenylurethane*, $C_{23}H_{35}O_2N$, m. p. 106—107°. Reduction of the sodium salt of ethyl tanacetophoronecarboxylate (compare A., 1912, i, 262) and treatment of the sodium compound of ethyl *iso*propyl*cyclo*pentanonecarboxylate thus obtained with diazobenzene chloride (1 mol.) in the cold, gives a clear, yellow solution from which sodium acetate precipitates a pale yellow product, gradually becoming darker. As would be expected from Dieckmann's work (A., 1901, i, 539), this represents 1-iso*propyl*cyclo*pentan*-3-*onephenylhydrazone*, $CHPr^{\beta}<\begin{matrix}C(:N_2HPh){\cdot}CO\\ CH_2\text{——}CH_2\end{matrix}$, which forms yellow crystals with metallic lustre, m. p. 233°; from acetic acid it separates in deep red crystals of somewhat lower melting point, the red colour being probably due to the formation of a condensation product. Treatment of 1-*iso*propyl*cyclo*pentan-3-one with zinc and ethyl bromoacetate in benzene gives the condensation product, $C_{16}H_{26}O$ (*vide supra*), and the ester of the oily hydroxy-acid, $C_{10}H_{18}O_3$. The action of acetic anhydride on this hydroxy-acid, followed by distillation in a current of water vapour, gives 1-iso*propyl*cyclo*pentylidene*-3-*acetic acid*, $CHPr^{\beta}<\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{\cdot}C{:}CH{\cdot}CO_2H\end{matrix}$, m. p. 107—108° (compare Wallach, "Terpene und Campher," II. ed., 160).

[With FRIEDRICH POHLE.]—Treatment of fencholenamine with

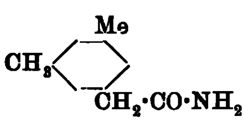
nitrous acid yields, in addition to hydrocarbons, not the primary unsaturated alcohol expected, but a tertiary *alcohol*, b. p. 90—93°/12 mm., probably 

Reduction of the latter in acetone by Paal's method gives *dihydrofencholene alcohol*, $C_{10}H_{19}$·OH, which is a pleasant-smelling oil, readily volatile in steam, b. p. 204—207°, or 95—96°/17 mm., D^{19} 0·898, n_D 1·4571; the latter is stable towards chromic acid, and by zinc chloride at 185—195° is converted into the *hydrocarbon*, $C_{10}H_{18}$, b. p. 165—167°, D^{20} 0·8035, n_D 1·4479. *Fencholenamine hydrate*, OH·C_9H_{16}·CH_2·NH_2, b. p. 134°/15 mm., or 112—113°/1—2 mm., gives, with sodium nitrite and acetic acid in the cold, a small yield of *dihydroxyfencholan*, $C_{10}H_{18}(OH)_2$, which sublimes in needles, m. p. 103—104°.

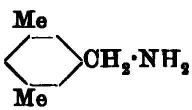
With nitrous acid, the amines of the type $[CH_2]_x>CH·CH_2·NH_2$ not only give the corresponding alcohols, but also undergo pronounced atomic rearrangement into alcohols of higher ring systems (compare Wallach, "Terpene und Campher," II. ed., 154 *et seq.*). In order to decide whether such rearrangement justifies the assumption of the presence of the unsubstituted group, ·CH_2·NH_2, or whether it occurs also in presence of the radicle, ·CHR·NH_2, the author has investigated the *base*, 

b. p. 193—194°, which is obtained by reduction of the oxime, m. p. 58—59°, prepared from 4-acetyl-1-methyl*cyclo*hexane (A., 1911, i, 472); the base forms a *carbamide*, m. p. 180—181°, and a *phenylcarbamide*, m. p. 98°, and with nitrous acid forms the corresponding secondary *alcohol*, 

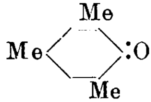
Condensation of 1:5-dimethyl*cyclo*hexen-3-one with zinc and ethyl bromoacetate, conversion of the hydroxy-ester thus obtained into the unsaturated acid, m. p. 153°, and reduction of the latter by Skita's method, gives 1 : 5-*dimethyl*cyclo*hexane-3-acetic acid*, $C_{10}H_{18}O_2$, b. p. 256—258°, or 137—139°/16 mm., D^{20} 0·962, n_D 1·4611, the *methyl* ester of which has b. p. 230—231°, or 116—118°/14 mm., D^{18} 0·9215, n_D 1·4476. This saturated acid was converted into the chloride and then into the *amide* (annexed formula), m. p. 141—143° or 146—148°, according to the character of the heating; the latter is always accompanied by the *nitrile*, $C_{10}H_{17}N$, b. p. 225°.



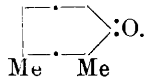
The action of bromine and alkali on the amide gives the *base* (annexed formula), which forms a *hydrochloride*, m. p. 240°, a *carbamide*, m. p. 154°, and an *acetyl* derivative, m. p. 79°. With sodium nitrite, the hydrochloride gives an oil, b. p. 195—205°, which yields a compound having the character of a cyclic ketone when oxidised with chromic acid; the *semicarbazone*, $C_{10}H_{19}ON_3$, of the ketone was prepared. An atomic displacement characteristic of aminomethyl-



cyclo-derivatives has therefore taken place. The ketone obtained may have either of the two structures



or

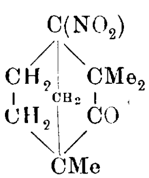


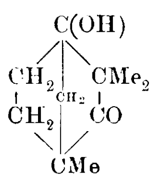
T. H. P.

[Mixtures of Phenol and Camphor in the Light of the Phase Rule]. R. KREMANN, F. WISCHO, and R. PAUL (*Monatsh.*, 1915, **36**, 911—921).—With a view to the explanation of the antiseptic properties of liquid mixtures of phenol and camphor, the authors have determined the freezing-point diagram. Mixtures containing from 25% to 60% of phenol could not be crystallised, but the curves actually realised suggest that a compound is formed, and this is supposed to be present in liquid mixtures (Chlumsky's solution). In agreement with previous observations, the freezing-point data for the system camphor–resorcinol show the existence of a compound. On the other hand, the freezing-point data for mixtures of camphor and β-naphthol, although incomplete, seem to show that no compound is formed by this pair of substances.

H. M. D.

Konovalov's "Hydroxyfenchone." S. S. NAMETKIN and (MLLE.) V. A. CHOCHRJAKOVA (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1611—1615).—It is a general rule that, when saturated, bicyclic hydrocarbons are nitrated by Konovalov's method, the tertiary hydrogen atom united to the carbon atom common to the two rings is not replaced by the nitro-group. In this connexion, interest attaches to Konovalov's observation (A., 1904, i, 257) that nitration of fenchone yields, besides a secondary nitro-ketone, also a tertiary nitro-compound, and that reduction of the latter yields mainly a compound of the composition $C_{10}H_{16}O_2$. If, as Konovalov assumed, this compound is formed from the tertiary nitro-derivative by replacement of the nitro-group by hydroxyl, these two compounds would have the annexed formulæ.





The authors have prepared the so-called hydroxyfenchone, b. p. 126·5—127°/11 mm., D_4^{20} 1·0028, n_D^{20} 1·4641, $[\alpha]_D$ −46·59° (in alcohol). This compound remains unchanged when heated with acetic anhydride or phthalic anhydride, and contains, therefore, no hydroxyl group. It yields, however, a *disemicarbazone*, $C_{10}H_{16}(N_2H{\cdot}CO{\cdot}NH_2)_2$, decomposing at 220°, and a *dioxime*, $C_{10}H_{16}(NOH)_2$, m. p. 123—124°, and is in reality a diketone, such structure being in excellent agreement with the molecular refraction. The simplest method of formation of such a compound would consist in a rupture, during

an intermediate stage of the reduction and under the influence of the strongly acid medium, of the bicyclic fenchone system at the carbon atom connected with the nitro-group. According to this view, the compound would have one of the two formulæ

$$CH_2<\begin{matrix} CO\text{---}CMe_2 \\ | \\ CMeEt\cdot CO \end{matrix} \quad \text{and} \quad \begin{matrix} CO\text{--}CH_2 \\ | \\ CH_2\cdot CH_2 \end{matrix}>CMe\cdot CO\cdot CHMe_2,$$

both of which represent optically active compounds. T. H. P.

Some [Japanese] Essential Oils. SO UCHIDA (*Bull. Forest. Expt. Stat. Meguro, Tokyo*, 1915. Reprint, 6 pp.).—*Hinoki oil* is obtained from the leaves and wood of the hinoki tree (*Chamaecyparis obtusa*), a valuable timber tree growing extensively in Japan. The wood yields 2·4% of the oil, which has a brown colour and empyreumatic odour. When rectified, the oil has $D^{15\cdot5}$ 0·8821 and $[\alpha]_D^{15}$ $-50\cdot61°$ (in a 10% chloroform solution). The oil contains about 60% of α-pinene and a considerable quantity of cadinene. The fraction of the oil b. p. (below) 170°/760 mm., and amounting to 60% of the total, is a good substitute for turpentine oil. *Sansho oil* has a strong aromatic odour, and is prepared from the berries of a shrub (*Xanthoxylum piperitum*) growing wild in Japan; it has $D^{15\cdot5}$ 0·8504, $[\alpha]_D^{20}$ $+46\cdot5°$, n_D^{20} 1·46, ester number 19·28, ester number after acetylation of the non-aldehyde constituent 23·23, and contains free acid (as palmitic acid) 2·0%, aldehyde 15%, esters (as acetic ester of $C_{10}H_{17}\cdot OH$) 5·7%, free alcohol ($C_{10}H_{17}\cdot OH$) 1·1%, and terpene (chiefly dipentene) 77·0%. This oil is useful for the preparation of perfumes, confectionery, liqueurs, etc. *Sugi oil* is obtained from the green leaves of the sugi tree (*Cryptomeria japonica*), a conifer indigenous to Japan; the yield of oil is 0·70%. The oil has $D^{15\cdot5}$ 0·9217, $[\alpha]_D^{15}$ $+19\cdot29°$, n_D^{20} 1·4985, acid number 1·0, ester number 6·56, and ester number after acetylation 14·35. The relative proportion of the constituents of the oil is as follows: free acid (as acetic acid), 0·1%; free *alcohol* ($C_{10}H_{17}\cdot OH$; b. p. 212—214°, n_D^{18} 1·4832), 3·14%; ester (as octoic ester of $C_{10}H_{17}\cdot OH$), 3·28%; terpene (chiefly α-pinene), 34%; sesquiterpenes, 30%; a sesquiterpene alcohol ($C_{15}H_{23}\cdot OH$; b. p. 284—286°, $D^{15\cdot5}$ 0·9623, $[\alpha]_D^{15}$ $+16\cdot76°$), 12%; *diterpene* (*α-cryptomerene*, m. p. 61°, b. p. 345°, $[\alpha]_D^{20}$ $-34\cdot22°$), 18%. W. P. S.

Action of Nitric Acid on Colophony and the Related Autooxidation of the Latter. LUDWIG PAUL (*Chem. Zentr.*, 1915, ii, 790; from *Seifensieder Zeit.*, 1915, **42**, 640—641, 659. Compare A., 1915, i, 828, 829, 1066).—The action of nitric acid on colophony proceeds even at the ordinary temperature. γ-Pinic acid (*KS* acid) yields a so-called nitro-product, m. p. 125—130°, whilst when diluted with water the product gives α-pinic acid (*KLw*), m. p. 100—105°. The action of nitric acid on finely divided colophony furnishes a substance, m. p. 120—125°, the nitro-compound separating as a yellow, pasty mass, which gives the *KLw*-substance, m. p. 135—136°, on treatment with water. Explosive

properties are not observed with the substances obtained by the action of nitric acid.

The nitro-compound obtained from γ-pinic acid is readily soluble in water containing sodium carbonate, and from the solution sodium chloride throws down a frothy precipitate very difficultly miscible with water. Addition of hydrochloric acid to the filtrate yields a yellow precipitate which is soluble in water, and, like β-pinic acid (β-*KLw*), has m. p. 120—125°; the residue from the extraction becomes transparent at 122°. Since both *KS* and colophony are almost free from β-pinic acid, the formation of the latter is attributed to the action of the nitric acid. If the use of sodium chloride is omitted from the preparation of α-pinic acid and the nitro-product is precipitated, the latter shows a considerably lower melting point; washing with water yields, not β-pinic acid, but a product resembling α-pinic acid. On the assumption that β-pinic acid is separated from the nitro-product if the initial product contains a considerable proportion of sodium chloride, whereas α-pinic acid is obtained when the oxidation ceases, owing to lack of hydrogen chloride or chlorine, the conclusion is drawn that the primary transformation product is α-pinic acid, which is only converted into the β-compound by oxidation. The basis of the auto-oxidation of colophony is not the latter itself, but α-pinic acid, which undergoes conversion into β-pinic acid. The α-compound is formed by treating colophony with alkali or nitric acid or by storing it in a closed vessel; nitration takes place only to a very subordinate extent. T. H. P.

Sphingosine. IV. Some Derivatives of Sphingosine and Dihydrosphingosine. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1916, **24**, 63—68).—The identification of sphingosine by the analysis of the sulphate is considered to be scarcely satisfactory on account of the inconstancy of the composition of this salt. On this account, the authors have prepared the picrate and picrolonate of sphingosine and dihydrosphingosine, but although these are of constant composition, their solubility in organic solvents is too great to make them very useful for the purpose of analysis.

Sphingosine picrolonate forms yellow crystals, m. p. 87—89° after softening at 81°.

Dibromosphingosine sulphate is a light grey, crystalline powder.

Dihydrosphingosine picrolonate forms long, yellow needles, m. p. 120—121° after softening at 110°. *Dihydrosphingosine picrate* forms yellow crystals, m. p. 88—89°.

It has already been shown (Levene and West, A., 1914, i, 308, 1123, 1141) that the probable structure of sphingosine is

$$C_{12}H_{25}\cdot CH{:}CH\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot NH_2,$$

the relative position of the amino- and hydroxyl groups being uncertain, but the isolation of *n*-pentadecoic acid as an oxidation product of dihydrosphingosine establishes the presence of a normal chain of fifteen carbon atoms. This knowledge is extended by the following observations.

On treating a solution of dihydrosphingosine sulphate in acetic

acid with the theoretical quantity of sodium nitrite, *dihydrosphingosol* (*trihydroxyheptadecane*), $C_{17}H_{33}(OH)_3$, is obtained as a colourless, crystalline solid, m. p. 54—55°.

When dihydrosphingosine sulphate in acetic acid solution is heated with hydriodic acid solution for five to seven hours, reduction is effected to *hydroxyheptadecylamine*, $OH\cdot C_{17}H_{34}\cdot NH_2$, scales, m. p. 85·5°; *sulphate*, rosettes of slender needles, m. p. 206—208° (compare Levene and Jacobs, A., 1912, i, 284, 575). D. F. T.

Sphingomyelin. III. P. A. LEVENE (*J. Biol. Chem.*, 1916, **24**, 69—89. Compare A., 1913, i, 917; 1914, i, 1147).—An extension of the earlier investigation to sphingomyelin obtained from kidney, liver, and the yolk of hen's egg.

Brain sphingomyelin prepared by a modification of the earlier method was obtained of constant composition and optical rotation. Hydrolysis by successive treatment with barium hydroxide and hydrochloric acid yielded lignoceric acid and another acid of lower molecular weight, possibly containing a hydroxyl group; no cerebronic acid was obtained, the occurrence of this acid amongst the products in the earlier investigation being probably due to the presence of cerebrin as an impurity in the sphingomyelin. The hydrolytic products included, as before, the bases choline, sphingosine, and the substance $C_{17}H_{35}ON$, the last, on reduction with hydrogen and colloidal palladium, yielding *sphingine* (hydroxyheptadecylamine) (compare Levene and West, preceding abstract), $OH\cdot C_{17}H_{34}\cdot NH_2$, plates, m. p. 83·5°, resembling cholesterol in appearance; sulphate, glistening scales; *diacetyl* derivative, needles, m. p. 109·5° (corr.). It is believed that the occurrence of this substance in the mixture obtained by reducing the hydrolytic products is due to a secondary formation of an anhydrosphingosine from sphingosine, because hydrolysis of sphingomyelin with 3% sulphuric acid in a sealed tube gave sphingosine without the new compound, whereas a sample of pure cerebrin, on successive treatment with barium hydroxide and sulphuric acid followed by reduction, gave pure sphingine. The primary hydrolytic products of sphingomyelin, therefore, are phosphoric acid, two fatty acids, choline, and sphingosine, and the constitution may be expressed $OH\cdot PO(O\cdot C_5H_{13}N\cdot OH)\cdot O\cdot C_{17}H_{33}(OH)\cdot NH\cdot CO\cdot C_{23}H_{47}$, the final acid radicle being uncertain. This assumption receives confirmation from the formation of *lignocerylsphingine*,

$$OH\cdot C_{17}H_{34}\cdot NH\cdot CO\cdot C_{23}H_{47},$$

needles, on reducing the hydrolytic products of sphingomyelin obtained from beef kidney.

Sphingomyelin was also prepared from liver and yolk of hen's egg. It is probable that the products from all these sources are identical. Whether sphingomyelin is a diphosphatide or a mixture of two phosphatides of the described type it is not possible to say; if it is a mixture, the proportion of the two monophosphatides present may vary according to the source of the material.

D. F. T.

Periodic Variation of the Properties of Organic Compounds. P. PETRENKO-KRITSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1796—1797).—Periodic variation of the melting point and of the reactivity is shown by the oximes of homologous compounds of the hydropyrone series (compare Biron, A., 1915, ii, 762). T. H. P.

The Alkaloids of the Calabar Bean. IV. Partial Synthesis of Eserine and Geneserine. MAX POLONOVSKI and CH. NITZBERG (*Bull. Soc. chim.*, 1916, [iv], **19**, 27—37. Compare A., 1915, i, 891, 892, 987).—The authors have examined the action of methylcarbimide on eseroline and geneseroline under varying conditions. For the preparation of eseroline from eserine, they now find that it is more satisfactory to use mineral acids instead of alkalis for the hydrolysis. The same applies to the preparation of geneseroline.

Methylcarbimide (1 mol.) reacts with eseroline (1 mol.) in benzene solution when heated in a sealed tube at 100° for four hours to give iso*eserine*, $(OH\cdot C_{13}H_{16}N)\colon N\cdot CO\cdot NHMe$, m. p. 195—196°, $[\alpha]_D$ $-236°$, in alcoholic solution. This substance is isomeric with eserine, but differs from it in several respects. Its aqueous solution is neutral, but it dissolves readily both in dilute acids and in dilute aqueous sodium hydroxide, the latter solution rapidly turning red on exposure to air. It gives a *picrate*, m. p. 170°, but no methiodide could be obtained. It is much more slowly decomposed by aqueous barium hydroxide than is eserine.

When methylcarbimide in benzene solution is added to a solution of eseroline in anhydrous ether in the cold, a precipitate of *eseroline methylcarbimide*, m. p. 110—115°, is obtained which, when heated at 110° for one hour, or dissolved in benzene and the solution warmed, is converted into *iso*eserine. When moistened with water it slowly dissolves, giving a yellow, alkaline solution which gradually turns red, and, on warming, drops of a red oil separate.

If in the second method of condensation of methylcarbimide and eseroline a small amount of sodium is introduced, then the product is eserine.

Attempts were made to add two methylcarbiminic groups to eseroline, one to the ·OH group and the other to a ·N atom, but no crystalline product could be obtained, although there was an indication that the reaction took place to a certain extent when the two substances were heated, in requisite proportions, in benzene solution in a sealed tube.

Geneserine was readily synthesised by the action of methylcarbimide on geneseroline in the presence of sodium by the method described above, but an *iso*geneserine could not be obtained from geneseroline using the first method given. W. G.

Preparation of Condensation Products of Papaverine and its Derivatives with Aldehydes or Substances Capable of Producing Aldehydes. SOCIÉTÉ POUR L'INDUSTRIE CHIMIQUE À BÂLE (Fr. Pat., 475654; from *J. Soc. Chem. Ind.*, 1916, **35**, 72).—Dihydropapaverine, tetrahydropapaverine, their substitution pro-

ducts, and the phenolic bases formed from them by the hydrolysis of one or more methoxy-groups, condense with aldehydes to form tetracyclic bases similar in constitution to some of the natural alkaloids. It is often preferable to use the acetal instead of the aldehyde, and saponify by a weak mineral acid. Details for the preparation of *methylene-* and *ethylidene-tetrahydropapaverine* and of *aminoethylidenetetrahydropapaverine hydrochloride* are given. G. F. M.

The Friedel-Crafts' Ketone Synthesis in the Pyridine Series. RICHARD WOLFFENSTEIN and FRANK HARTWICH (*Ber.*, 1915, **48**, 2043—2049).—The authors have found that pyridine and quinoline and their derivatives cannot be condensed with acetyl or benzoyl chloride in the presence of aluminium chloride, and that no reaction takes place, on the other hand, between pure pyridinecarboxylic acid chlorides and aromatic hydrocarbons or ethers. If, however, a trace of thionyl chloride is also used with the condensing agent, ketones are readily obtained. Sufficient thionyl chloride will remain with the acyl chlorides if, in the preparation of these, the excess is removed merely by evacuation at the room temperature.

The necessary acids were obtained by oxidising the alkylpyridines, and it is stated that pyridine-2:6- and 2:5-dicarboxylic acids can be readily purified by crystallisation from water without the usual intervention of the silver salts. Another difference is brought to light between the 3- and 4-acids and pyridine-2-carboxylic acid (picolinic acid). The chloride of the latter condenses with pyridine to give a deep cornflower-blue dye, which, however, soon decomposes.

The following ketones are described: 2-Pyridyl phenyl ketone, from picolinoyl chloride and benzene, b. p. 182°/14 mm. (compare Tschitschibabin, A., 1902, i, 175); platinichloride, m. p. 193° (decomp.). 2-*Pyridyl anisyl ketone*, $C_{13}H_{11}O_2N$, long, silky needles, m. p. 93°; *platinichloride*, m. p. 210° (decomp.); *picrate*, m. p. 176°; *phenylhydrazone*, pale brown, m. p. 103°. 3-Pyridyl phenyl ketone, b. p. 180°/12 mm., m. p. 39°; platinichloride, m. p. 245° (decomp.) (compare Bernthsen and Mettegang, A., 1887, 737). 3-*Pyridyl anisyl ketone*, soft needles, m. p. 99°; *platinichloride*, m. p. 267° (decomp.); *picrate*, m. p. 185°; *phenylhydrazone*, pale yellow nodules, m. p. 157°. 3-*Pyridyl naphthyl ketone*, a brown resin; *platinichloride*, m. p. 213° (decomp.); *picrate*, m. p. 142°. 2:5-*Dibenzoylpyridine*, spikelets, m. p. 123°; *platinichloride*, unstable; *diphenylhydrazone*, $C_{31}H_{25}N_5$, m. p. 129°. 2:6-*Dibenzoylpyridine*, a very weak base, m. p. 108°; *diphenylhydrazone*, m. p. 183°. J. C. W.

Isomeric Phenylmethyl*iso*oxazolecarboxylic Acids. MARIO BETTI and REMO PACINI (*Gazzetta*, 1915, **45**, ii, 377—384).—The action of hyroxylamine on ethyl benzoylacetoacetate (compare Claisen, A., 1894, i, 32) yields a phenylmethyl*iso*oxazolecarboxylic

acid, m. p. 189° (compare A., 1915, i, 713), isomeric with the acid, m. p. 157°. It is now found that the amide of 5-phenyl-3-methyl*iso*oxazole-4-carboxylic acid, obtained by oxidation of 4-benzylidene-3-methyl*iso*oxazolone in presence of benzaldehyde, yields mainly the acid, m. p. 157°, or that with m. p. 189°, according as it is boiled with dilute or concentrated sodium hydroxide solution. Further, just as is the case with the ester of 3 : 5-diphenyl*iso*oxazole-4-carboxylic acid (compare Betti and Berlingozzi, A., 1915, i, 997), the ester obtained by the interaction of hydroxylamine and ethyl benzoylacetoacetate yields solely the acid, m. p. 189°, when hydrolysed by either concentrated or dilute sodium hydroxide solution. In some instances the corresponding salts of the two acids exhibit marked differences. The nature of the isomerism of these acids is not yet established. T. H. P.

Nitro-derivatives of Alkyl Benzidines. G. van Romburgh (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 757—760).—The compounds obtained earlier by the nitration of dimethylaniline, and described as *iso*dinitrodimethylaniline and dinitrophenylmethylnitroamine (Mertens, A., 1886, 1022), were shown by van Romburgh (A., 1887, 245) to be derivatives of tetranitrobenzidine.

Details are now given by which the yield of tetranitrotetramethylbenzidine obtained from dimethylaniline by nitration can be very considerably improved. The method of formation from dimethylaniline suggests that the nitro-groups occupy the 3 : 5 : 3′ : 5′-positions, and this view is now confirmed in the following way.

4 : 4′-Diphenyl diethyl ether when treated with fuming nitric acid was converted into the tetranitrodiphenyl diethyl ether, colourless needles, m. p. 256—257°. When heated with an alcoholic solution of dimethylamine at 120°, this substance gave tetranitrodihydroxydiphenyl, a result that helped to fix the positions of the nitro-groups, because on boiling with nitric acid this compound was converted into picric acid. With methylamine, tetranitrodiphenyl diethyl ether gave 3 : 5 : 3′ : 5′-tetranitrodimethylbenzidine, decomp. at 282°, and the proof of the structure of this substance by synthesis also applies to the above tetranitrotetramethylbenzidine and its derivatives.

By allowing other monoalkylamines to react with the tetranitrodiphenyl diethyl ether, the corresponding *ethyl*, *propyl*, iso*propyl*, iso*butyl*, and *allyl* compounds were obtained, m. p. (decomp.) 248°, 202°, 250°, 194°, 208° respectively, which were convertible into the corresponding *nitroamines*, m. p. 230°, 213°, 209°, 205°, 100° respectively.

Tetranitrotetramethylbenzidine and tetranitrodimethylbenzidine are both slowly reducible by tin and hydrochloric acid, giving *tetra-aminotetramethylbenzidine* and *tetra-aminodimethylbenzidine*; *tetrahydrochlorides*, needles with $2H_2O$ and $1H_2O$ respectively; *stannichlorides*, crystalline scales. D. F. T.

Diazotisation and Diazo-reactions of 2-Aminopyridine. A. E. TSCHITSCHIBABIN and M. D. RJAZANCEV (*J. Russ. Phys. Chem. Soc.*, 1915, **46**, 1571—1589. Compare A., 1915, i, 590, 591, 992). —By treating 2-aminopyridine with nitrous acid in hydrochloric acid solution, the authors were unable to obtain a higher yield than 50% of 2-chloropyridine, much 2-pyridone being always formed (compare Marckwald, A., 1893, i, 727; 1894, i, 381). Use of concentrated hydrofluoric acid in place of the hydrochloric acid results in the formation of 2-fluoropyridine in about 25% yield. In the case of hydrobromic acid, the concentrated acid cannot be employed, since it reacts with nitrous acid, liberating bromine; with more dilute solutions, 2-bromopyridine is obtained in small yield, the principal product being the pyridone. It is evident that 2-aminopyridine reacts considerably more slowly than aromatic amines with nitrous acid. The extraordinarily great stability of pyridyl-2-nitroamine leads the authors to suppose that, with 2- and 4-substituted pyridines, only the salts of the diazonium bases are unstable, whilst the diazo-compounds, $C_5H_4N{\cdot}N{:}N{\cdot}ONa$, and also the nitroso-amines, $C_5H_4N{\cdot}NH{\cdot}NO$, should be at least as stable as the corresponding compounds of the aromatic series. The application of Bamberger and Rüst's reaction (A., 1901, i, 171) to 2-aminopyridine yields the *iso*diazoxide, which may also be obtained by the action of amyl nitrite on the sodium derivative of 2-aminopyridine; it is extremely stable, and in the pure state remains unchanged indefinitely, only decomposing at a high temperature. Decomposition of a concentrated aqueous solution of the diazoxide (1 mol.) in the cold with not more than 1 mol. of acetic acid yields the crystalline diazo-hydrate, which, however, readily decomposes with formation of pyridone; the slightest excess of acid results in the rapid decomposition of the diazoxide, which probably undergoes isomeric change into the unstable diazonium salt. Faint acidification of a solution of the diazoxide containing potassium iodide yields 2-iodopyridine. Like the *anti*diazoxides of the benzene series, the diazoxide of pyridine exhibits little tendency to the formation of azo-dyes by coupling with phenols and amines; small yields of such dyes are, however, obtainable with naphthols and certain amines in alcoholic solution. The assumption concerning the stability of diazoxides or nitrosoamines of the 2-pyridine series is also confirmed by other experiments. Thus, in absence of other acids, nitrous acid gives with 2-aminopyridine aqueous solutions which generate nitrogen either slowly or not at all, and are capable of yielding products of the diazo-reaction.

2-*Fluoropyridine*, C_5H_4NF, is a volatile liquid with an odour resembling that of 2-chloropyridine, b. p. 125·75°/752·9 mm., D_0^0 1·1489, D_0^{20} 1·1281, n_D^{20} 1·4678. It forms either no salt or a highly unstable one with picric acid. The extreme weakness of the basic properties is shown also by the fact that the *platinichloride*, $(C_5H_4NF)_2,H_2PtCl_6+H_2O$, m. p. 145—153° (decomp.), loses water and hydrogen chloride at 100°, giving $(C_5H_4NF)_2PtCl_4$.

2-Pyridone exhibits dimorphism, crystallisation from hot chloro-

form or benzene giving large, prismatic crystals, which gradually assume a milky, opaque appearance. Its sodium salt shows marked stability towards air and light.

Sodium pyridine-2-diazoxide, $C_5H_4N\cdot N\colon N\cdot ONa$, is obtained as a pale yellow powder.

2-*Iodopyridine*, C_5H_4NI, is a liquid, b. p. 93°/13 mm., D_0^0 2·0039, D_0^{20} 1·9735, n_D^{20} 1·6366; its *picrate*, $C_{11}H_7O_7N_4I$, m. p. 119—120°, and *platinichloride*, $(C_5H_4NI)_2,H_2PtCl_6$, red needles, m. p. 210° (decomp.), were prepared. T. H. P.

Nitrates of Aminoazo-compounds. L. CASALE (*Gazzetta*, 1915, **45**, ii, 397—405).—In conjunction with Casale-Sacchi (A., 1915, i, 723), the author has described two series of nitrates of various aminoazo-compounds, stable salts containing 1 mol. of nitric acid and unstable ones 2 mols. of nitric acid per 1 mol. of the base. It is now shown that, under the action of heat or, in one case, even at the ordinary temperature, all these salts are decomposed with liberation of the diazonium salt, which serves to prepare the colouring matter, and formation of a nitro-derivative of the amine. An analogous decomposition was observed with the nitrates of hydroxyazo-compounds by Charrier and Ferreri (A., 1914, i, 599, 748), and termed by them "diazo-scission." The explanation of this reaction advanced by these authors, and extended by Charrier (A., 1915, i, 66) to the nitrates of aminoazo-compounds, does not seem to be in accordance with the facts. Indeed, almost all nitrates of aminoazo-compounds containing 2 mols. of acid to 1 mol. of the base dissociate spontaneously at the ordinary temperature, losing gradually 1 mol. of nitric acid. With 4-*o*-tolueneazo-1-naphthylamine nitrate this decomposition takes place especially rapidly and with generation of heat; in other cases the change is readily brought about by gentle heating. That such decomposition occurs under the influence of heat is regarded as a proof of the invalidity of Charrier and Ferreri's hypothesis, since heat can only displace from left to right the equilibrium of the system, nitrate of the azo-compound $\rightleftarrows$ azo-compound + nitric acid. The author considers the decompositions of the two types of nitrates to be represented thus: (1) $NAr\colon N\cdot Ar\cdot NH_2,2HNO_3 = NAr\colon N\cdot Ar\cdot NH_2 + 2HNO_3 = NO_2\cdot Ar\cdot NH_2 + NO_3\cdot NAr\colon N + H_2O$, and (2) $2NAr\colon N\cdot Ar\cdot NH_2,2HNO_3 = 2NAr\colon N\cdot Ar\cdot NH_2 + 2HNO_3 = NO_2\cdot Ar\cdot NH_2 + NO_3\cdot NAr\colon N + NAr\colon N\cdot Ar\cdot NH_2$. The thermal decomposition of the nitrates of the azo-compounds thus consists in the action of concentrated nitric acid on the azo-compounds; this action was studied by Schmidt (A., 1905, i, 951), who, however, wrongly supposed that three or more mols. of nitric acid act on 1 mol. of the azo-compound. The investigations have been extended to the nitrates of dimethylaminoazobenzene and *p*-tolueneazo-β-naphthylamine.

Dimethylaminoazobenzene forms the two *nitrates*: (1) $C_{14}H_{15}N_3,2HNO_3$, which forms a deep blood-red, crystalline precipitate, and (2) $C_{14}H_{15}N_3,HNO_3$, which forms large, violet, rhombic plates and loses its colour at about 110°, its melting point being

that of the free base. Salt (1) undergoes almost quantitative, and salt (2) somewhat less complete, decomposition into phenyldiazonium salt and 4-nitro-1-dimethylaminobenzene, when heated.

p-Tolueneazo-β-naphthylamine gives two nitrates:

$$(1)\ C_6H_4Me{\cdot}N{:}N{\cdot}C_{10}H_7{\cdot}NH_2,2HNO_3,$$

which forms deep, garnet-red prisms with metallic lustre, and is stable in cold, dry air; and (2) $C_{17}H_{16}N_3,HNO_3$, which forms shining, green crystals. When heated, these salts yield *p*-tolyldiazonium nitrate and 1-nitro-2-naphthylamine, small or quantitative yields being obtained according to the way the heating is carried out.

Similar results have been obtained with the nitrates of benzene-azo-α-naphthylamine, 4-*o*- and 4-*m*-tolueneazo-1-naphthylamine, *p*-tolueneazo-α-naphthylamine, 4-*o*-methoxy- and 4-*o*-ethoxy-benzene-azo-1-naphthylamines, and 4-naphthaleneazo-1-naphthylamine.

T. H. P.

The Formation of Pyridine and *iso*Quinoline Bases from Casein. AMÉ PICTET and TSAN QUO CHOU (*Compt. rend.*, 1916, **162**, 127—129).—The authors have hydrolysed 50 grams of casein by heating it on a water-bath with 150 grams of hydrochloric acid (D 1·19) for six hours, whilst adding 25 grams of methylal, drop by drop, during the operation, the hydrolysis of the casein being thus effected in the presence of a permanent source of formaldehyde. The liquid was then evaporated to dryness, the residue mixed with three times its weight of calcium oxide, and distilled. The distillate was a yellow oil, entirely soluble in dilute hydrochloric acid, and containing primary, secondary, and tertiary bases. The tertiary bases were freed from the others by treatment with sodium nitrite and fractionally distilled. From the different fractions the following bases were isolated and characterised: Pyridine, 2:6-dimethylpyridine; a *base*, C_7H_9N, isomeric with this, which decolorised potassium permanganate in the cold and gave a *picrate*, m. p. 238°, an *aurichloride*, m. p. 225°, a *mercurichloride*, m. p. 235°, and a *platinichloride*, m. p. 285°; *iso*quinoline; 4-methyl*iso*quinoline; a *base*, $C_{11}H_{11}N$, probably an ethyl- or a dimethyl-*iso*quinoline, giving a *picrate*, m. p. 240°, and *aurichloride*, m. p. 195°, and a *platinichloride*, m. p. above 300°; a *base*, $C_{12}H_{13}N$, giving a *picrate*, m. p. 185°. They could not discover the slightest trace of quinoline.

W. G.

Pure Pepsin. W. E. RINGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 738—751. Compare Pekelharing and Ringer, A., 1911, i, 1051).—The theoretical portion of the paper is mainly directed against the views of Michaelis and his co-workers (Michaelis and Davidsohn, A., 1910, i, 795; Michaelis and Mendelssohn, A., 1914, i, 1007).

Pure pepsin, free from chlorine and phosphorus, was obtained by Pekelharing's method from the gastric juice of a dog. Whether dissolved in pure water or in an aqueous solution of sucrose it does not exhibit an isoelectric point, as stated by Michaelis and Davidsohn (*loc. cit.*), but is always electronegative, tending to

move towards the anode if in an electric field. In the presence of albumoses, however, the behaviour of the pepsin may be so modified as to give indications of an isoelectric point, and this is probably the explanation of the mistake of other investigators. Certain of the author's results confirm the view that pepsin may be a combination of a real enzyme and protein; thus under electrical stress in acid solution the enzyme constituent appears to move towards the anode whilst most of the protein matter migrates towards the cathode; also in hydrochloric acid solution, pepsin combines chiefly with hydrogen ions, refuting the hypothesis that the whole of the material consists of enzyme which is known to be invariably charged negatively through combination with anions.

Experimental examination also disposes of the suggestion (*loc. cit.*) that the action of pepsin depends entirely on the concentration of the hydrogen ion. Tests made with different acids lead to the conclusion that the optimum for the digestion of the fibrin is situated at the point of maximum swelling; this maximum does not lie at the same hydrogen-ion concentration for different acids, but depends on the nature of the anion. With an acid such as sulphuric acid, containing a very hydrophilous anion, the effect of the latter is so marked that it prevails even in comparatively dilute solution, so that the maximum swelling is small, and concurrently the digestion is relatively inappreciable, the optimum occurring at a low concentration of hydrogen ion. The relation between digestion and swelling of fibrin is even more distinctly shown in the influence of various salts. If a list of sodium salts is drawn up in the order of their inhibitory effect on swelling, it is found that the power of impeding the action of pepsin falls in the same order. To avoid as far as possible any effect of the salts on the concentration of the hydrogen ion, lactic acid was selected for the experiments, the dissociation of this acid being only slightly influenced by the addition of the salts chosen. D. F. T.

The Total Nitrogen and α-Amino-nitrogen of Pepsins of Different Strengths. T. B. Aldrich (*J. Biol. Chem.*, 1915, **23**, 339—343).—Various pepsins examined showed wide variations in activity. In the different samples total nitrogen showed very little variation, but what did vary was the α-amino-nitrogen, the decrease in percentage of which runs parallel with an increase in the activity; pepsin, therefore, seems to approach the proteins in complexity. W. D. H.

The Effects of Electrolytes, Non-electrolytes, Alkaloids, etc., on the Urease of Soja-bean. Naosuke Onodera (*Biochem. J.*, 1915, **9**, 544—574).—The inhibitory effects of acids depend mainly on hydrogen-ion concentration, and also on the effect on surface tension; these have a great effect on surface tension, and facilitate the adsorption of hydrogen ions on the surface of the urease particles. The inhibitory effect of sodium hydroxide is ascribed to hydroxyl-ion concentration, but ammonia has some further action. $1M$-methyl, ethyl, propyl, and $M/40$-amyl alcohols accelerate urease

activity; but 3·3M of the former group and M/12-amyl alcohol retard it. Isocapillary alcohol solutions have equal effects. Osmotic pressure (Traube's capacity factor) will not explain these effects, but the intervention of attraction pressure represented here by surface tension (Traube's intensity factor) will. The alcohols do not cause dispersion or aggregation of urease particles. Aldehyde inhibits urease notably. The actions of neutral salts are merely those of their metallic bases. Alkaloid salts accelerate urease action in the first stage of hydrolysis, but the alkaloid bases themselves inhibit markedly. The effects of atropine and pilocarpine are additive, not antagonistic. W. D. H.

The Urease of the Soja-bean and its Coenzyme. NAOSUKE ONODERA (*Biochem. J.*, 1915, **9**, 575—590).—The soja-bean urease loses its activity on dialysis; this is restored by adding a small amount of fresh urease, which indicates that the latter contains coenzyme. The coenzyme was not separated nor its nature known; but it probably consists of two components, one of which is dialysable, the other not; the former undergoes some irreversible change during dialysis. It also consists of fixed and free parts; heating and dialysis destroy the free part first, and then the fixed part; the last portion of the fixed coenzyme is found in the precipitate produced by dialysis, and it resists the influence of heat and dialysis tenaciously. The inhibitory effects of heat, acid, and alkali are exerted on the coenzyme, not on the urease proper. During germination, urease accumulates in the germ of the bean, but free coenzyme is absent. Ox-serum has an accelerating influence, but this is small compared with that of the coenzyme. W. D. H.

Influence of the Bromine-ion on Uricolysis. ANTONIO JAPPELLI (*Chem. Zentr.*, 1915, ii, 965; from *Arch. Farmacol. sperim.*, 1915, **19**, 529—534).—The presence of sodium bromide in isotonic solution inhibits the oxidation of uric acid by pressed liver juice. This action on the uricase of the liver is a special case of the antifermentative properties of the bromine ion. T. H. P.

Preparation of Arseno-phosphorus Derivatives. A. MOUNEYRAT (Eng. Pat., 1915, 9234; from *J. Soc. Chem. Ind.*, 1916, **35**, 72).—Arseno-phosphorus compounds are obtained by the action of phosphoryl chloride on *m*-amino-*p*-hydroxyphenylarsinic acid in presence of aqueous sodium hydroxide, and subsequent reduction with sodium hyposulphite. These compounds, the composition of which varies with the proportions of the original reagents, form yellow powders, soluble in dilute sodium carbonate solution and in hydrochloric acid, and their alkaline solutions reduce Fehling's solution and Nessler's and Tollen's reagents. They are only slightly toxic, but have marked spirillicidal and trypanosomicidal properties. G. F. M.

A Method of Preparing Mercurised Aromatic Alcohols. V. GRIGNARD and A. ABELMANN (*Bull. Soc. chim.*, 1916, [iv], **19**, 18—25).—Whilst it has been possible to obtain mercury derivatives

of hydrocarbons, phenols, amines, acids, sulphonic acids, ketones, etc., by the action of mercuric oxide, chloride, or acetate (compare Dimroth, A., 1899, i, 154, 428; 1902, i, 656), up to the present no such derivatives of aromatic alcohols have been obtained, but these have now been prepared indirectly from the mercurised ketones by the action of organo-magnesium compounds. The two ketones used were acetophenone and benzophenone, their mercury compounds being condensed with magnesium ethyl bromide.

ω-Chloromercuriacetophenone has been prepared by the method of Dimroth and Ilzhöfer (compare A., 1902, i, 849), a small amount of o-ω-*dichloromercuriacetophenone* being found to be present in the product. *o*-Chloromercuribenzophenone was prepared as described by Dimroth and Metzger (compare A., 1902, i, 849), and the authors at the same time isolated a small amount of *dichloromercuribenzophenone*, $CO(C_6H_4{\cdot}HgCl)_2$. ω-Chloromercuriacetophenone when condensed with the calculated quantity of magnesium ethyl bromide gave a solid product and an ethereal solution. The solid product when purified by crystallisation from chloroform was shown to be *α-chloromercuri-β-phenylbutan-β-ol*,

$$OH{\cdot}CPhEt{\cdot}CH_2{\cdot}HgCl,$$

m. p. 129—131° (decomp.). It reacted vigorously with magnesium ethyl bromide, gave a precipitate of mercuric sulphide with ammonium sulphide, and with concentrated sulphuric acid gave a green coloration, which disappeared on the addition of water. The ethereal solution yielded a small amount of a *compound*, m. p. 138—139° (decomp.), which exhibited all these properties, and was shown to be *o*-chloromercuriphenylchloromercurimethylethyl carbinol (α-chloromercuri-β-*o*-chloromercuriphenylbutan-β-ol), $HgCl{\cdot}C_6H_4{\cdot}CEt(OH){\cdot}CH_2{\cdot}HgCl$. *o*-Chloromercuribenzophenone when condensed with magnesium ethyl bromide gave *α-phenyl-α-chloromercuriphenylpropan-α-ol*, $OH{\cdot}CPhEt{\cdot}C_6H_4{\cdot}HgCl$, m. p. 106° (decomp.), which exhibits the above properties, except that it is not attacked by ammonium sulphide in the cold. W. G.

Physiological Chemistry.

Thrombin and Calcium Chloride in Relation to Coagulation. JOHN OGLETHORPE WAKELIN BARRATT (*Biochem. J.*, 1915, **9**, 511—543).—A given amount of thrombokinase in presence of calcium chloride and prothrombin will produce a definite quantity of thrombin, which is independent of the concentration of prothrombin. The coagulation time is concerned with the action of thrombin (y) on fibrinogen (z); when decinormal calcium chloride is present (0·05 in 5 c.c.), $xy=nz$, where x is the coagulation time and n a constant. If more calcium chloride is added to snake venom thrombin, or to a mixture of thrombokinase and prothrom-

bin, coagulation is retarded. If the coagulation time is plotted against the amount of calcium chloride employed, the points up to a critical limiting value lie on a parabola given by the equation $w^2 = ax - b$. Of the two constants a is proportional to the amount of thrombokinase, and b is a function of z not yet determined. The action of thrombin on fibrinogen takes place according to the equation $w^2 = p(xy/z - n)$, where n is a constant independent of w, xy, or z, and p is a function of z not yet determined. Minimal quantities of calcium chloride accelerate the coagulant activity of the thrombin of the venom of *Echis carinatus*. W. D. H.

The Effect of the Ingestion of Urea, Sodium Lactate, and Sodium Hydrogen Carbonate on the Reaction of the Blood and the Composition of the Alveolar Air in Man. GORO MOMOSE (*Biochem. J.*, 1915, **9**, 485—491).—These three substances in the doses taken by the mouth produce little change in the alveolar carbon dioxide, but cause an appreciable increase in the affinity of blood for oxygen in the presence of carbon dioxide, which is the result of the increased alkalinity of the blood. Five-gram doses of sodium lactate do not appreciably affect the percentage saturation of the blood with oxygen in the presence of the alveolar pressure of carbon dioxide. W. D. H.

The Fixation of Salvarsan and Neo-salvarsan by the Blood after Intravenous Injection. WILLIAM JOHN YOUNG (*Biochem. J.*, 1915, **9**, 479—484).—After intravenously injecting goats with these substances, the serum contains arsenic in a form which cannot be separated from the proteins by dialysis, and is precipitated with the serum proteins by tannic acid. Salvarsan and neo-salvarsan therefore behave like atoxyl. No such combination is obtained when inorganic arsenic is injected. This combined arsenic is found in the plasma, and in the red blood corpuscles, but no trace of it is retained in the fibrin. W. D. H.

The Influence of Salicylates on the Elimination of Uric Acid and other Waste Products from the Blood. W. DENIS (*J. Pharm. expt. Ther.*, 1915, **7**, 255—262).—From a study of cases of disease in which salicylates were employed, it is found that the increase of uric acid in the urine is due to a lowered "threshold" value of the kidney; this probably applies to other waste products also. In rheumatism the beneficial effect is ascribed to this circumstance; the increase of kidney permeability facilitates a rapid excretion of the unknown toxins which produce rheumatic symptoms. W. D. H.

The Effect of Organ Extracts on Gastric Secretion. JOHN ROGERS, JESSIE M. RAHE, GEORGE G. FAWCETT, and GEORGE S. HACKETT (*Amer. J. Physiol.*, 1916, **39**, 345—353).—Hypodermic injection of the non-coagulable portion of aqueous extracts of thyroid, parathyroid, thymus, spleen, and liver stimulate gastric secretion and mobility, but those of the pituitary and suprarenal

inhibit the flow. Both the coagulable and non-coagulable portions of pancreatic extracts stimulate the flow. All these substances appear to act on some peripheral gastric mechanism in which the nervous system is an essential part. W. D. H.

The Influence of Carbohydrate and Fat on Protein Metabolism with Special Reference to the Output of Sulphur. KWANJI TSUJI (*Biochem. J.*, 1915, **9**, 439—448).—Three experiments on a dog are recorded in which extra nitrogen in the shape of caseinogen, egg-albumin, and gelatin respectively were superimposed on a basal diet; nitrogen retention was greater on a carbohydrate than on a fat diet. The same holds for sulphur, except in the caseinogen experiment. The actual amounts of extra nitrogen and sulphur excreted vary with the protein used, but the extra sulphur is mainly excreted as inorganic sulphate. The partition of the sulphur in the carbohydrate and fat diets is very similar, namely, nearly equal parts of inorganic sulphates and "neutral sulphur." There is no evidence that the protein retained is poor in sulphur. W. D. H.

The Use of Phloridzinised Dogs to Determine the Utilisable Carbohydrate in Foods. The Food Value of Commercial Glucose. W. D. SANSUM and R. T. WOODYATT (*J. Biol. Chem.*, 1916, **24**, 23—30).—The total dextrose which any given food may introduce into the metabolism will depend on (1) the free dextrose it contains, (2) the amount of other carbohydrates capable of conversion into dextrose within the body, and (3) protein digestion products. Food analysis alone is often incapable of giving the necessary data. The method suggested is to give the food to phloridzinised dogs, and the extra sugar found in the urine would represent nothing which is either indigestible, unabsorbable, or unassimilable; nitrogen estimation would give a measure of the sugar derived from protein. In the present experiments pure dextrose given by the mouth did not appear quantitatively in the urine; some may be destroyed in the bowel by bacteria; this may be excluded by subcutaneous administration, and by this means a higher figure (86%) was obtained; with commercial glucose the average figure was 71·3, as compared with 74·6 for the average of the pure dextrose experiments. It is possible some sugar may be burnt in the body, or elimination by the kidneys may be imperfect. The more freely the kidneys act, the more sugar is obtained. W. D. H.

The Stability of the Growth-promoting Substance in Butter-fat. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1916, **24**, 37—40).—Previous work has shown that this substance in butter-fat (especially abundant in the oil fraction) is unaffected by heat. The present experiments show that storage for some months or even a year in the case of butter-fat has no effect, but in the butter-oil gradual deterioration occurred, so that its characteristic potency was almost completely lost within a year. W. D. H.

Ionic Antagonism in Sensory Stimulation. W. J. CROZIER (*Amer. J. Physiol.*, 1916, **39**, 297—302).—The experiments consisted in noting the reaction times in brainless frogs, their feet being placed in mixtures of the chlorides of sodium, potassium, and calcium. Sodium chloride ($0{\cdot}5M$) is a weak but measurable stimulant; sea-water does not stimulate. The mixtures of the salts demonstrate antagonism between them. In normal stimulation the essential step includes the penetration of the surface layer of the receptor by the stimulant. W. D. H.

Secretion of the Pituitary by Stimulation of the Superior Cervical Ganglion. V. N. SHAMOFF (*Amer. J. Physiol.*, 1916, **39**, 279—290).—The experiments recorded indicate that stimulation of the superior cervical sympathetic ganglion in the cat leads to a discharge of pituitary secretion which produces diuresis and glycosuria. The acceleration of the flow of urine is independent of the elevation of blood-pressure. W. D. H.

The Effect of Phloridzin on the Formation of Glycogen in the Liver. ALBERT A. EPSTEIN and GEORGE BAEHR (*J. Biol. Chem.*, 1916, **24**, 17—21).—After removal of the kidneys, phloridzin increases the hepatic glycogen. The drug is believed to stimulate this function of the liver; but if the kidneys are intact, the glycosuric action of phloridzin is so much more powerful that the accumulations of glycogen in the liver are rapidly diminished. On removal of the kidneys, however, the glycosuric action is eliminated, so that the effect on the liver becomes manifest even in a state of starvation. W. D. H.

The Action of Pituitary Extracts on Isolated Intestinal Loops. V. N. SHAMOFF (*Amer. J. Physiol.*, 1916, **39**, 268—278).—Differences were noted in various commercial preparations of pituitary extract (posterior lobe), but some of them are capable of producing relaxation of the isolated intestinal loop (rabbit) and of inhibiting its rhythmic contractions, resembling in this respect extracts of the adrenal medulla. The substance responsible for the effect is probably different from that which raises blood pressure and produces diuresis. W. D. H.

Salicylaldehyde and Diphenols in the Investigation of the Oxidising Power of Animal Organs. LEOPOLDO LÓPEZ-PÉREZ (*Anal. Fis. Quim.*, 1915, **13**, 453—460).—The author's experimental results indicate the presence in human tissue of a catalyst capable of oxidising catechol, quinol, and salicylaldehyde, its activity being conditioned by the nature of the medium in which the action takes place. A. J. W.

The Resistance of Fresh-water Fish to Changes of Osmotic and Chemical Conditions. WALTER E. GARREY (*Amer. J. Physiol.*, 1916, **39**, 313—329).—The fish *Notropis blennius* will live for months in St. Louis tap-water, which is distinctly alkaline. They

will also live in redistilled water for weeks. Sucrose is directly toxic to them, but least so when present in osmotic equilibrium; this toxicity is reduced by salts and alkalis. Chlorides of the following metals are toxic in this order: K > Mg > Ca > Na. One chloride (except that of potassium) reduces the toxicity of the others. When three or four are present, the solutions become less toxic still. Sea-water diluted to the concentration of the blood (or less) is a perfectly balanced solution for these fresh-water fish. Above this concentration, death is prompt. W. D. H.

The Influence of Fat and Carbohydrate on the Excretion of Endogenous Purines in the Urine of Dog and Man. NOBUYOSHI UMEDA (*Biochem. J.*, 1915, **9**, 421—438).—From experiments on himself, it is clearly shown that the protein-sparing action of carbohydrate is greater than that of fat. A diet rich in carbohydrate causes a formation of uric acid, as in the dog it increases the allantoin. Glycerol is a protein sparer and increases the output of endogenous uric acid; the latter effect is also caused by sodium hydrogen carbonate. In several experiments the increase of uric acid is associated with a fall in the purine bases excreted. With diets rich in fat but poor in carbohydrates the uric acid output is decreased. In dogs, sodium lactate raises the output of allantoin. W. D. H.

Acidosis. ROBERT MILNE LANG (*Biochem. J.*, 1915, **9**, 456—478). —On an ordinary diet, the author excreted daily 10—30 mg. of acetone substances. After fasting, carbohydrate, and to a less degree protein and glycerol, reduce the acidosis, but fat increases it. Alcohol has no effect. The amount of acetone substances in the urine of the first few days of starvation depends on the initial carbohydrate storage; when the ratio of the fat to carbohydrate present becomes greater than 2 to 1, these substances appear in abnormal amount, and are for the most part derived from fat. Some evidence of the formation of carbohydrate from fat in the body is adduced. W. D. H.

So-called "Protective Enzymes." Antitryptic Index and Anaphylaxis. IX. J. BRONFENBRENNER (*Proc. Soc. Expt. Biol Med. New York*, 1915, **13**, 42—43).—The symptoms of eclampsia, epilepsy, and asthma recall anaphylaxis. There is considered to be in these conditions a casual relation between the condition of the blood and these diseases. The antitrypsin of the blood is increased; this allows the proteolytic enzyme there to act, and results in autodigestion of the serum and the production of toxic material. W. D. H.

The Output of Creatine in Glycosuria. KWANJI TSUJI (*Biochem. J.*, 1915, **9**, 449—455).—The injection of adrenaline in a dog caused glycosuria, creatinuria, and a rise in output of total nitrogen. In the same animal, ether anæsthesia had similar effects. In the estimation of creatine, due care was taken not to confuse it with acetoacetic acid. W. D. H.

Experimental Diabetes after Pancreatectomy. ALBERT A. EPSTEIN and GEORGE BAEHR (*J. Biol. Chem.*, 1916, **24**, 1—16).—In experimental diabetes after pancreatectomy in cats, the volume of the blood alters, and this change must be allowed for in estimating variations in sugar, nitrogen, and other constituents of that fluid. The hyperglycæmia after the removal of the pancreas mounts progressively in the terminal stages, because the permeability of the kidney is less; this explains why in diabetic coma the blood-sugar rises so greatly. If both kidneys are removed the same result ensues; the accumulation of sugar in the blood is largely due to the mobilisation of carbohydrate from the liver and muscles. W. D. H.

Production of Pneumonia by Intrabronchial Insufflation of Unorganised Substances. B. S. KLINE and S. J. MELTZER (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 29—30).—Non-virulent pneumococci introduced by insufflation produce pneumonia which macroscopically resembles that caused by virulent organisms. Aleuronat and starch produce pneumonia like that caused by virulent pneumococci; egg-yolk and lecithin produce pneumonia like that caused by non-virulent cocci. Egg-white has no such effect. W. D. H.

Accumulation of Nitrogen in the Tissues in Renal Disease. HELEN DAVIS and NELLIS B. FOSTER (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 33—35).—Data of nitrogen-retention in the tissues are given. In nephritis there is a notable increase in the extractive nitrogen in muscle and liver, but when œdema was present the results were inconstant. In other conditions without nephritis, for instance pneumonia, there was a similar accumulation of nitrogen. W. D. H.

A Toxic Substance in the Blood of Uræmic Patients. NELLIS B. FOSTER (*Proc. Soc. Expt. Biol. Med. New York*, 1915, **13**, 39).—Uræmia blood yields a substance of unknown nature which is fatal to guinea-pigs; this is absent in normal blood. W. D. H.

Mode of Action of Ultra-violet Radiation on Living Cells, especially in the Eye. W. E. BURGE (*Amer. J. Physiol.*, 1916, **39**, 335—344).—Ultra-violet radiation (especially between 254 and 302 $\mu\mu$) affects protoplasm in such a way that certain salts combine with it to form an insoluble compound or coagulum. An opacity of the lens can be produced in fishes living in solutions of these salts (calcium chloride, sodium silicate) which are greatly increased in human cataract if the eyes are exposed to radiation from a quartz mercury-vapour burner. Abnormal quantities of these salts in the cells of the eyelids and cornea increase the effectiveness of ultra-violet rays in causing this eye trouble. In the skin they increase the effectiveness of short wave-lengths in producing sunburn. W. D. H.

The Comparative [Physiological] Action of the Stereoisomerides of Hydroxyhydrindamine. YASUO IKEDA (*J. Pharm. expt. Ther.*, 1915, **7**, 121—124).—The hydroxyhydrindamines have no specific action, but are mild general protoplasmic poisons. The *d*-compound is very slightly more toxic than the *l*-compound

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Rate of Growth of Bacteria. ARTHUR SLATOR (T., 1916, **109**, 2—10).—It is shown that the rate of growth of bacilli which produce a silky turbidity in the medium can be estimated by comparing the solutions with suspensions of asbestos in water. The organism employed produces lactic acid, and occurs in malt-wort. When an active growth in wort was obtained, it was matched against one of the standard asbestos suspensions and then diluted with fresh wort to dilutions of 1/100 to 1/100,000. The rate of growth cannot be ascertained from the rate of production of lactic acid, as growth is retarded by even small amounts of acid. When, however, two quantities of wort are seeded, the seeding in one case being considerably larger than in the other, the development of acidity in the first case occurs earlier than in the second; the rate of growth is calculated from the difference in time and the ratio of the seedings.

Measurements were made at different temperatures (22—55°) at which growth is possible and in different concentrations of wort. In the latter experiments it was found the growth was the same when D varied between 1·060 and 1·008.

Most of the lactic acid is produced when the development is greatly retarded, as even 5·6° acid lowers the rate of growth.

N. H. J. M.

Quantitative Investigations on Indole and Tryptophan Decomposition. E. HERZFELD and R. KLINGER (*Centr. Bakt. Par.*, 1915, i, **76**, 1—12).—The negative indole reaction which is observed in cultures of certain bacteria has been attributed to their supposed inability to decompose tryptophan. The authors show that this view is not correct, and that when comparatively large quantities of bacteria, for example, *B. typhosus* and *B. paratyphosus B.*, are brought into pure tryptophan solution, a considerable proportion (20—60%) of the compound is destroyed without any accumulation of indole. Under similar conditions, such organisms as *B. coli* and *Vibrio cholerate* produced up to 55% of indole.

The absence of indole from "indole-negative" cultures is explained, in the case of the typhoid and paratyphoid organisms, by

the fact that these bacteria have a well-marked capacity of decomposing indole either in the pure state or in the presence of small quantities of peptone. The presence of certain sugars or of large quantities of peptone tends to decrease the production of indole by *B. coli* and to prevent tryptophan decomposition by *B. typhosus* and *B. paratyphosus B.* H. B. H.

The Lipoids of the Blastomycetes. A. AMATO (*Centr. Bakt. Par.*, 1915, ii, **42**, 689—698).—Fixed preparations of *Saccharomyces ellipsoideus* when treated with osmic acid show only a few granules which reduce osmic acid, and therefore exhibit black coloration, whilst the majority of the granules assume a brown colour. On the basis of differential coloration and their behaviour towards fat solvents after being acted on by osmic acid, the majority of the granules in the yeast are looked on as belonging to the class regarded by Bernard and Bigart as labile fats.

By comparison with the rate and type of coloration of a number of pure compounds, the assumption is made that the majority of the lipoids in yeasts consist of lecithin. Extraction of the washed and dried yeast by means of ether gave a residue which, on combustion and subsequent extraction with sodium nitrate and sodium carbonate, gave the characteristic phosphoric acid precipitate with ammonium molybdate. The behaviour of certain other cell granules towards neutral-red is also described, but no conclusions are drawn as to their nature and function. H. B. H.

Nitrogenous Constituents of Yeast. JAKOB MEISENHEIMER (*Chem. Zentr.*, 1915, ii, 1259; from *Woch. Brauerei*, 1915, **32**, 325—326).—The author has investigated the products of the autolysis of pure cultures of top and bottom fermentation yeasts in presence of toluene. From the cell residues, phytosterol, m. p. 156—157°, was isolated. The remaining mass was dissolved completely in boiling hydrochloric acid, and from the solution thus obtained glucosamine hydrochloride was deposited in the crystalline form. The following amino-acids were detected and their proportions estimated by Fischer's ester process: glycine, alanine, valine, leucine, proline, phenylalanine, aspartic and glutamic acids, tyrosine, and tryptophan; the presence of serine, cystine, and an aminobutyric acid was not demonstrated with certainty. The proportion of tryptophan from a top yeast containing 6·6% N and 92·4% of dry matter amounted to 0·30%, and that from a bottom yeast containing 6·7% N and 83·4% dry matter to 0·34% of the dry matter. T. H. P.

Action of Ultraviolet Rays on Alcoholic Fermentation. ROMOLO DE FAZI and REMO DE FAZI (*Ann. Chim. Applicata*, 1915, **4**, 301—329).—A summary is given of the investigations of various authors on the effect of ultraviolet light on micro-organisms. The experiments now described lead to the following conclusions. The action of ultraviolet rays, even when exerted for a comparatively long time, is favourable to alcoholic fermentation. Beer yeast

undergoes marked increase in activity when exposed to ultraviolet rays for a definite length of time, and is not killed by an exposure lasting for fourteen hours. This action of ultraviolet rays serves as a means of selection of yeast. These results differ from that of Henri, Helbronner, and Recklinghausen, who found that, with an artificial mixture of yeast and sarcina, the latter is completely destroyed by an exposure of thirty seconds to ultraviolet light, whilst the yeast is only attacked after the exposure has lasted thirty minutes. T. H. P.

Culture of Aspergillus niger (Sterigmatocystis nigra) in Liquids in which the Zinc is Replaced by Different Elements (Copper, Uranium, Vanadium). M. JAVILLIER (*Chem. Zentr.*, 1915, ii, 1051; from *Bull. Sci. Pharmacol.*, 1914, **21**, 452—463. Compare A., 1913, i, 235; 1914, i, 119).—When present in sufficient proportion, copper produces an appreciable increase in the weight of the mycelium of this organism, and is fixed by it, the under side assuming a more or less intense blue coloration. The copper also accelerates the formation of conidia and intensifies their colour. This influence of copper on spore formation is also evident when zinc is present in the nutrient solution; the two metals together effect a greater acceleration in the growth of the mould than either separately. Uranium appears to be without appreciable influence on *Aspergillus niger.* Vanadium increases the yield of mycelium—in one case by more than 40%; this effect may, however, be due partly to the sulphur of the vanadium sulphate employed. In presence of vanadium and zinc together, the amount of mycelium formed is somewhat greater than with zinc alone. Neither copper nor vanadium, used in any proportion or for any length of time, can accelerate the growth or increase the yield of mycelium to even approximately the same extent as zinc in proportions between $1 . 10^{-7}$ and $0·5 . 10^{-6}$. T. H. P.

Fluorine in the Vegetable Kingdom. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1916, **162**, 105—112. Compare A., 1912, ii, 681, 805, 806; 1913, i, 677, 789, 1017).—The authors have determined the percentages of fluorine and phosphorus in a large number of plants or parts of plants, which serve as food for human beings and herbivora, with a view to discovering how fluorine passes from the plant to the animal. The results, which are set out in detail, show that, in plants, the leaves are the organs which are richest in fluorine, the proportion of phosphorus being also generally high as compared with the rest of the plant. The buds, as in cauliflowers and asparagus, are slightly less rich in fluorine, although the phosphorus content of asparagus buds is remarkably high. The stems, wood, and bark are the organs which are poorest both in fluorine and phosphorus. Edible roots, such as carrots and radishes, contain very variable proportions of fluorine and phosphorus. Soft fruits are moderately rich in fluorine and phosphorus, the pulp being poorer in fluorine than the skin. In seeds, the fluorine content is medium and comparable to that of the

pulp of fruits. In the case of cereals, granitic soils favour an increase of fluorine in the flour. The bran of wheat is very poor in fluorine, but very rich in phosphorus. The flour from cereals generally resembles the pulp of fruit in being moderately rich in phosphorus, whilst in the seeds of leguminosæ the phosphorus content is high. The results do not indicate any particular plant-group where fluorine is particularly abundant and necessary. For the different organs of the same plant there is apparently no simple law governing the ratio of fluorine to phosphorus, but they increase and diminish together. W. G.

The Displacement by Water of Nitrogenous and Mineral Substances Contained in Leaves. G. André (*Bull. Soc. chim.*, 1915, [iv], **17**, 429—441).—For the most part a more detailed account of work already published (compare A., 1913, i, 233). The experiments have been repeated with another year's crop of chestnut leaves, somewhat more in detail, and the results obtained confirm those already published (*loc. cit.*). W. G.

A New Method for the Preparation of the Plant Globulins. George Reeves (*Biochem. J.*, 1915, **9**, 508—510).—Sodium chloride solutions are usually employed to extract the plant globulins, but the yield is usually small. Schryver showed that globulins are much more soluble in salt solutions which lower surface tension, and this forms the basis of the new method recommended, a semi-normal solution of sodium benzoate being the one which gave the best results. In this way 130 grams of crude edestin were prepared from 450 grams of hemp seed sifted meal; and 30 grams of excelsin from 250 grams of Brazil-nut meal. Legumin and vicillin were similarly obtained from horse beans, and separated by Osborne's method. W. D. H.

Evodin. a Crystallised Substance Present in the Fruit of Evodia Rutaecarpa. Y. Asahina and M. Ishio (*J. Pharm. Chim.*, 1916, [vii], **13**, 53; from *Yakugakuzassi*, 1915).—The dried fruits of *Evodia rutæcarpa* possess an aromatic odour and a bitter taste, and have long been used in China and Japan in medicine and perfumery. In 1902, Keimatzu extracted a crystallisable substance from the fruits by means of benzene; the crystals had m. p. 285°, were insoluble in water, alcohol, ether, and light petroleum, slightly soluble in hot benzene, ethyl acetate, and chloroform, and soluble in acetic acid and in alkali solutions. The authors have further investigated this substance, to which the name *evodin* has been given. They find that, owing to the readiness with which it oxidises and polymerises, it can be separated from the fruit as a pure substance only by distillation with steam; it has the formula $C_{17}H_{20}O_6$. Besides evodin, the fruits contain a considerable quantity of other crystallisable substances which constitute a complex mixture containing more than 10% of nitrogen. W. P. S.

Chemistry of Heterotrophic Phanerogams. II. F. WOSOLSOBE and J. ZELLNER (*Monatsh.*, 1915, **35**, 1511—1532. Compare Zellner, A., 1914, i, 913).—In extension of the earlier investigation the authors have submitted to chemical examination, not only tobacco-plants affected by *Orobanche Muteli* and *Orobanche ramosa*, but also the parasitic growths themselves and healthy plants. The materials in each case were dried, and the analysis was made on the dried substance.

In the case of *Orobanche Muteli*, examination was made of the ash, the extracts obtained from the dry material with light petroleum, ether, alcohol, and water respectively, and the insoluble residue. The roots of healthy and affected plants were examined in a similar manner. The results show that the composition of *Orobanche Muteli* may vary appreciably with the position of the plant affected, but the most notable feature is the relatively high content of soluble substances, such as potassium salts, dextrose, and mannitol in the parasite; it appears probable that the osmotic pressure of these compounds assists in the extraction of sap from the roots of the plants. Nicotine does not pass as such into the parasitic growth. The thickened portion of the stem of the parasite appears to serve for the storage of starch produced from the soluble carbohydrate compounds removed from the parent plant. The affected tobacco root may lose very considerably in weight, and shows a reduction in its content of potassium salts, starch, and, to a smaller extent, nitrogenous compounds. It is also observed that even with healthy roots the content of soluble substances varies considerably with the season, climate, and position.

It is believed that the food of the parasite is not drawn directly from the root, but that the latter merely acts as an organ by which food can pass from the soil and from the stem and leaves to the parasite. Although the root may be affected by this disturbance of its functions, it does not necessarily follow that it will always be very seriously affected.

The case of the *Orobanche ramosa* was not so closely investigated, but the results indicated a relationship between plant and parasite similar to that described above. D. F. T.

Beetroots Attacked by Cercospora beticola sacc. ÉMILE SAILLARD (*Compt. rend.*, 1916, **162**, 47—49).—The beetroot crop of 1915 was attacked by the fungus *Cercospora beticola sacc.*, with the result that the crop was poor in quantity and quality, although the sugar content, with a few exceptions, was as high as in an average year. The juices were less pure and contained more salts. Reckoned as a percentage of the sugar, the beetroots contained more total, amino-, ammoniacal, and injurious nitrogen than in previous years, even the dry year of 1911. Further, there was decided loss of sugar, more remaining in the molasses. The roots contained a dextrorotatory substance other than sucrose, which was not precipitated by lead acetate, but which disappeared along with the amino- and ammoniacal nitrogen during the manufacturing process. W. G.

Connection between Absorption and Coagulation and its Influence on the Soil. A. DE DOMINICIS (*Chem. Zentr.*, 1915, ii, 1307; from *Staz. sperim. agrar. ital.*, 1915, **48**, 525—535. Compare A., 1915, i, 859).—The results of experiments made in conjunction with G. GANGEMI lead to the following conclusions: The recognition of the relation between absorption and coagulation, and its bearing on the chemistry of the soil, is of considerable importance. The two phenomena proceed together, and a change in one is always accompanied by a simultaneous, analogous change in the other. Thus, for instance, the coagulating powers of different ions correspond with their degrees of absorption. Absorption effects a retrogression of the colloids, a diminution of the difference of electrical potential between the contrasted phases, and a rise in the surface tension, the phenomenon of coagulation thus making its appearance.

T. H. P.

Amino-acid Nitrogen of Soil R. S. POTTER and R. S. SNYDER (*J. Ind. Eng. Chem.*, 1915, **7**, 1049—1053).—The work of Chardet (A., 1915, i, 762), who found by the Sörensen method 49—68% of the soil nitrogen to be amino-acid nitrogen, was not confirmed. By the Kober method of estimation (A., 1913, ii, 990), no amino-acid nitrogen could be found in the acid extract of soil even if amino-acids were previously added, but after one hour's extraction with dilute alkali practically the whole of the amino-acid nitrogen was removed. A typical analysis of a soil containing 0·151% of total nitrogen by the alkali extraction method and estimation according to Kober gave 7·95 parts of amino-acid nitrogen and 31·5 parts of peptide nitrogen per million. From pot experiments with variously treated soils, the conclusion was drawn that there is no tendency for amino-acid nitrogen to accumulate in either a limed or an unlimed acid soil, whether manured or not, and although the heavily manured soils showed a decided decrease in nitrate nitrogen at first there was a marked increase after from four to six weeks. Amino-acid nitrogen was present in less amount than ammonia nitrogen, but it fluctuated in general with the latter.

G. F. M.

Characterisation of Soils by means of Hydrochloric Acid Extracts and by the Power of Exchanging Bases. ALEXIUS A. J. VON SIGMOND (*Bied. Zentr.*, 1915, **44**, 433—438; from *Intern. Mitt. Bodenk.*, 1915, **5**, 165).—The classification of soils by means of hydrochloric acid extracts, and estimations of the liberated silicic acid dissolved by hot, saturated sodium carbonate solutions, is discussed (compare Mitscherlich, *ibid.*, 1914, **4**, 327).

N. H. J. M.

Organic Chemistry.

New Methods of Obtaining Divinyl, Isoprene, Piperylene, and Dimethylerythrene. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1947—1978).—Isoprene may be obtained by the following methods: (1) Depolymerisation of natural myrcene, $CH_2:CMe\cdot CH_2\cdot CH_2\cdot CH:CH\cdot CMe:CH_2 = 2CH_2:CMe\cdot CH:CH_2$; (2) dehydration of $\beta\delta$-dihydroxy-β-methylbutane,

$$OH\cdot CMe_2\cdot CH_2\cdot CH_2\cdot OH = 2H_2O + CH_2:CMe\cdot CH:CH_2;$$

(3) removal of 2HCl from $\beta\delta$-dichloro-β-methylbutane by means of quinoline or other amines,

$$CMe_2Cl\cdot CH_2\cdot CH_2Cl = 2HCl + CH_2:CMe\cdot CH:CH_2;$$

(4) removal of 1HCl from monochloro*iso*amylenes by means of sodium stearate, $CMe_2:CH\cdot CH_2Cl = HCl + CH_2:CMe\cdot CH:CH_2$; (5) removal of acetic acid from δ-acetoxy-β-methyl-Δ^{α}-butene,

$$CH_2:CMe\cdot CH_2\cdot CH_2\cdot OAc = C_2H_4O_2 + CH_2:CMe\cdot CH:CH_2;$$

(6) depolymerisation of the terpenes, dipentene, limonene, pinene, etc., $CMe{<}{\genfrac{}{}{0pt}{}{CH{-}CH_2}{CH_2\cdot CH_2}}{>}CH\cdot CMe:CH_2 = 2CH_2:CMe\cdot CH:CH_2$; (7) action of zinc dust on $\alpha\beta\gamma\delta$-tetrabromo-β-methylbutane,

$$CH_2Br\cdot CMeBr\cdot CHBr\cdot CH_2Br + 2Zn = 2ZnBr_2 + CH_2:CMe\cdot CH:CH_2.$$

$\beta\gamma$-Dimethylerythrene may be obtained by: (1) depolymerisation of the cyclic dihexene, $CMe{<}{\genfrac{}{}{0pt}{}{CMe\cdot CH_2}{CH_2{-}CH_2}}{>}CMe\cdot CMe:CH_2 = 2CH_2:CMe\cdot CMe:CH_2$; (2) dehydration of pinacone by means of sulphanilic acid or salts of phosphoric acid, $OH\cdot CMe_2\cdot CMe_2\cdot OH = 2H_2O + CH_2:CMe\cdot CMe:CH_2$. For the preparation of piperylene, see this vol., A., i, 4.

Tilden observed that dipentene is depolymerised at 400—600° into isoprene, and the author finds that pyrogenetic decomposition of homologues of dipentene yields homologues of isoprene, cyclic dibutene being converted into erythrene, $C_8H_{12} = 2C_4H_6$, and cyclic dihexene into $\beta\gamma$-dimethylerythrene, $C_{12}H_{20} = 2C_6H_{10}$ (compare Lebedev, A., 1913, i, 1285). When heated at 150—250°, limonene is converted into polyterpenes of high boiling point, whereas at 500—600° it yields isoprene, and the increased yield of the latter obtained by Staudinger and Klever (A., 1911, i, 731) is due, not to dilution of the limonene vapour, but to the high temperature at which this vapour is formed; good results are obtained when the limonene is mixed with benzene, toluene, xylene, light petroleum, etc. The pyrogenetic decomposition of turpentine yields isoprene and also gases and liquid hydrocarbons distilling between 60° and 150°; these hydrocarbons may be used in place of benzene, etc., as a diluent. Pyrogenetic decomposition of saturated hydrocarbons and of hydrocarbons containing one double linking yields only erythrene, no homologues of the latter being obtained: $C_4H_8RR' = CH_2:CH\cdot CH:CH_2 + R'H + RH$, or $C_4H_7R = CH_2:CH\cdot CH:CH_2 + RH$; natural myrcene gives isoprene in 60—70% yield.

The conversion of $\beta\delta$-dichloro-β-methylbutane into erythrene by the action of an amine takes place only when the basicity of the amine is relatively weak; in the case of primary amines, this weakening of the basic properties may be effected by the introduction of radicles into the molecule. In this reaction, quinoline, *p*-chloro- and *p*-bromo-aniline, and tetramethyldiaminobenzophenone are converted into colouring matters of basic character which behave as indicators. When heated with quinoline, both δ-chloro-β-methyl-Δ^{α}-butene and δ-chloro-β-methyl-Δ^{β}-butene yield isoprene, the dimethylallene first formed in the latter case undergoing isomeric change; when the quinoline is replaced by sodium stearate, such isomeric change does not take place, isoprene being obtained from the first, and dimethylallene from the second, of the above chloro-derivatives. When heated with lime, sulphanilic acid, or alkali alkyloxide, δ-acetoxy-β-methyl-Δ^{α}-butene gives no trace of isoprene, but under the influence of alumina at 380—450° a yield of 20% of isoprene is obtainable. The dehydration of *iso*amylene glycol to isoprene takes place under the same conditions as that of 1 : 3-*iso*-butylene glycol; alumina and also phosphoric acid were used as dehydrating agents (compare Lebedev, *loc. cit.*).

The results obtained on heating hydrocarbons of different types lead to the following general rule: Open-chain hydrocarbons containing one ethylenic linking in the molecule, or saturated cyclic hydrocarbons, lose at high temperatures mostly saturated hydrocarbons, all the carbon atoms being expelled with the exception of four, which remain in the form of erythrene. The latter may, indeed, be obtained from almost any hydrocarbon containing not fewer than four carbon atoms in the molecule, thus: $C_nH_{2n+2} + Cl_2 = HCl + C_nH_{2n+1}Cl$; $C_nH_{2n+1}Cl = C_4H_8RCl =$
$HCl + RH + CH_2\colon CH\cdot CH\colon CH_2$.

T. H. P.

Conversion of the *cyclo*Butane Derivatives, Bromo*cyclo*butane and *cyclo*Butanol, into Erythrene. Mechanism of the Removal of Different Radicles from the 1- and 4-Positions. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1978—1982).—The fact that the action of zinc dust on $\alpha\delta$-dibromo-Δ^{β}-butene yields erythrene, according to the equations,

$$(1)\ CH_2Br\cdot CH\colon CH\cdot CH_2Br + Zn = ZnBr_2 + CH{<}{}^{CH}_{CH_2}{>}CH_2$$

and (2) $CH{<}{}^{CH}_{CH_2}{>}CH_2 = \left\{\begin{matrix} CH\cdot CH_2 \\ | \\ CH\cdot CH_2 \end{matrix}\right\} = CH_2\colon CH\cdot CH\colon CH_2$, leads to the conclusion that reactions yielding *cyclo*butene should, owing to isomerisation of this hydrocarbon, give also erythrene. The author has confirmed this conclusion by obtaining erythrene (1) by the scission of hydrogen bromide from bromo*cyclo*butane, and (2) by the scission of water from *cyclo*butanol. Similar results were obtained by Willstätter and Schmaedel (A., 1905, i, 514), who prepared erythrene by the removal of bromine from 1 : 2-dibromo*cyclo*butane, and obtained a mixture of *cyclo*butene (about 90%) and erythrene (about 10%) on complete methylation of amino*cyclo*-

butane, $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2}\\\mathrm{CH_2}\end{matrix}>\mathrm{CH\cdot NMe_3\cdot OH} = \mathrm{CH_2}<\begin{matrix}\mathrm{CH=}\\\mathrm{CH_2}\end{matrix}>\mathrm{CH} + \mathrm{NMe_3} + \mathrm{H_2O}$, and by Willstätter and Bruce (A., 1907, i, 1018), who obtained $\Delta^{\alpha\gamma}$-butadiene by the removal of ammonia from amino*cyclo*butane. Thus, the reactions expressed by the following two equations may be regarded as general methods for the preparation of erythrene:

(1) $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2}\\\mathrm{CH_2}\end{matrix}>\mathrm{CHR} = \mathrm{RH} + \mathrm{CH_2{:}CH\cdot CH{:}CH_2}$, and

(2) $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2}\\\mathrm{CHR}\end{matrix}>\mathrm{CHR'} = \mathrm{RH} + \mathrm{R'H} + \mathrm{CH_2{:}CH\cdot CH{:}CH_2}$.

For instance, monosubstituted alkyl-, alkoxy-, or acetyl-*cyclo*butane should give erythrene either when heated or when treated with a suitable catalyst; under similar conditions, derivatives of homologues of *cyclo*butane should yield the corresponding homologues of erythrene; thus, 1- or 2-methyl*cyclo*butanol should give methylerythrene.

Perkin found that, when heated, *cyclo*butene-1:2-dicarboxylic acid is converted into the anhydride of an acid, the structure of which was not established. According to the above considerations, the anhydride thus formed must be that of dimethylenesuccinic acid,

$$\begin{array}{l}\mathrm{CH_2\cdot C\cdot CO_2H}\\ \quad | \qquad |\\ \mathrm{CH_2\cdot C\cdot CO_2H}\end{array} = \left[\begin{array}{l}\mathrm{CH_2\cdot C\cdot CO_2H}\\ \qquad \times|\\ \mathrm{CH_2\cdot C\cdot CO_2H}\end{array}\right] = \begin{array}{l}\mathrm{CH_2{:}C\cdot CO_2H}\\ \qquad |\\ \mathrm{CH_2{:}C\cdot CO_2H}\end{array} =$$

$$\begin{array}{l}\mathrm{CH_2{:}C\cdot CO}\\ \qquad | \\ \mathrm{CH_2{:}C\cdot CO}\end{array}\!\!>\mathrm{O}.$$

T. H. P.

Analysis, Purification, and Qualitative Reactions of Isoprene. Structure of the Benzene Nucleus. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1983—1988).—The formation in a reaction of a diolefine with conjugated double linkings may be detected by shaking 5—10 drops of the products of the reaction for a short time with 50 c.c. of concentrated aqueous sulphurous acid, the mixture being then left at the ordinary temperature in a hermetically sealed vessel. In the course of two to thirty hours, an abundant, colourless, amorphous precipitate is formed, this consisting of a compound of the diolefine with the sulphur dioxide and possessing characteristic properties (compare Badische Anilin- & Soda-Fabrik, A., 1911, i, 938).

Isoprene may be estimated by converting it into $\beta\delta$-dichloro-β-methylbutane, 70·49 grams of the latter corresponding with 34·03 grams of isoprene. The procedure is as follows: 200 grams of the crude isoprene, containing butylenes, amylenes, benzene, etc., are shaken vigorously for six hours with 1500 c.c. of fuming hydrochloric acid. The black, opaque upper layer of chloro-compounds is separated by means of a separating funnel, washed with aqueous sodium chloride solution saturated in the cold, again separated after the emulsion formed has divided into two layers, dried over calcium chloride, and distilled. At 40—50° only two or three drops of

hydrocarbons usually distil over, and the fraction 50—90° contains butylene and amylene chlorides; the fraction 90—130° is collected separately. From 130° the temperature generally rises immediately to 142°, the boiling point of βδ-dichloro-β-methylbutane. When the crude isoprene has been obtained from turpentine, the βδ-dichloro-β-methylbutane cannot be distilled, but it is found that the residue in the distilling flask with b. p. beyond 143° consists, in spite of its black colour, of almost chemically pure βδ-dichloro-β-methylbutane; in a vacuum, indeed, this residue distils completely within 0·5° of the proper temperature. This residue may be filtered through glass-wool and the filtrate weighed. The fraction, b. p. 90—130°, is subjected to careful fractional distillation, as it contains βδ-dichloro-β-methylbutane, sometimes in considerable quantity.

A method is described for the purification of crude isoprene containing turpentine, benzene, amylenes, etc.

When heated with sodium, chemically pure isoprene yields an abnormal caoutchouc differing considerably in its properties from the sodium–isoprene caoutchouc described first by Matthews and Strange, and later by Harries.

The author regards the stability of halogen atoms combined with the nucleus of aromatic compounds as due to the presence in this nucleus of three double linkings, the halogen always being attached to a carbon atom possessing such a linking. On this assumption, those chemical agents which react with the halogen of an aromatic nucleus should also react with the halogen of vinyl haloids. The halogen of bromobenzene reacts readily, in presence of ether, with either sodium or magnesium, and it has been shown by Prshebytek (A., 1889, 362) that, in presence of ether, sodium easily removes bromine from β-methylvinyl bromide, $2CHMe\colon CHBr + 2Na = 2NaBr + CHMe\colon CH\cdot CH\colon CHMe$, and by Austerweil (A., 1912, i, 525) that sodium or magnesium acts on vinyl bromide in the same way as on bromobenzene. The conclusion is drawn that benzene is a hydrocarbon with conjugated linkings, and is confirmed by the behaviour of aromatic compounds in various reactions. Thus, hydrogen unites at the conjugated linking of an open-chain compound, and also, as in the partial hydrogenation of phthalic acids, with the benzene nucleus in the 1- and 4-positions. Further, pyrogenetic reactions yield erythrene and benzene with almost identical ease and often in identical proportions. With barium peroxide, amylenes react with almost explosive violence, whereas isoprene is quite passive towards this reagent; this marked stability to oxidising agents is closely analogous to that exhibited by aromatic compounds. Benzene may be regarded as the cyclic analogue of erythrene, $\begin{array}{c}CH\colon CH\cdot CH\colon CH\\ \llcorner\!-CH\colon CH-\!\lrcorner\end{array}$. T. H. P.

Transference of the Elements of Halogen Hydracid from One Organic Radicle to Another. Mechanism of the Action of Chlorine on Trimethylethylene [β-Methyl-Δ^{β}-butene]. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1988—1991).—The author shows that the first stage of the action

of chlorine on β-methyl-Δ^{β}-butylene (compare Kondakov, A., 1885, 736; 1886, 136) results in the formation of a dichloride of the latter. This dichloride is then converted into chloro*iso*amylene by loss of the elements of hydrogen chloride, which unite with a further molecule of β-methyl-Δ^{β}-butylene: (1) $C_5H_{10} + Cl_2 = C_5H_{10}Cl_2$; (2) $C_5H_{10}Cl_2 + C_5H_{10} = C_5H_9Cl + C_5H_{11}Cl$. Whether the elements of hydrogen chloride are lost from β-methyl-$\beta\gamma$-dichlorobutane, $CMe_2Cl{\cdot}CHMeCl$, or from an unstable dichloro-derivative in which the two chlorine atoms retain their "molecular" linkings and which may be formed as a transient intermediate product, is not yet decided. T. H. P.

Preparation of Ethyl Bromide. ALFRED HOLT (T., 1916, **109**, 1—2).—In order to obtain a good yield of ethyl bromide from sodium or potassium bromide, it is necessary to use a large quantity of a mixture of water, alcohol, and sulphuric acid, and to distil at as low a temperature as possible (compare Weston, A., 1915, i, 1049). The author employs a mixture of 1500 c.c. of concentrated sulphuric acid, 900 c.c. of water, 1500 c.c. of alcohol, and 1200 grams of potassium bromide (or an equivalent of $NaBr,2H_2O$). The ingredients are mixed carefully in the cold, and distilled for eight or nine hours. The yield is 90—96% calculated on the bromine, and the product contains no hydrogen bromide and is almost free from ether, as revealed by a density measurement. J. C. W.

Interaction of Tetranitromethane and Potassium Ferrocyanide. FREDERICK DANIEL CHATTAWAY and JOHN MALTHOUSE HARRISON (T., 1916, **109**, 171—174).—A saturated aqueous solution of potassium ferrocyanide reacts quietly and quantitatively with tetranitromethane and bromotrinitromethane, but not with chloro- or bromo-picrin, to form the potassium salt of *aci*-trinitromethane, thus: $C(NO_2)_4 + 2K_4FeC_6N_6 = C(NO_2)_2{:}NO{\cdot}OK + KNO_2 + 2K_3FeC_6N_6$, and $C(NO_2)_3Br + 2K_4FeC_6N_6 = C(NO_2)_2{:}NO{\cdot}OK + KBr + 2K_3FeC_6N_6$. This affords a safe and easy way of preparing the *aci*-trinitromethane salt, whereas the older method, the action of potassium ethoxide on tetranitromethane, is very risky (Macbeth, A., 1913, i, 1146). J. C. W.

The Preparation of Anhydrous Ethyl Alcohol. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1916, **29**, 18).—Commercial calcium shavings contain appreciable quantities of calcium nitride, so that when used for the dehydration of alcohol the latter is liable to contain ammonia. When used as follows, however, this difficulty is obviated. The shavings are sieved with a fine sieve, thus removing most of the calcium nitride, after which they are washed with dry carbon tetrachloride (or other suitable liquid) to remove traces of petroleum. For every litre of alcohol, 20 grams of these cleaned shavings are used. In order to remove ammonia from the anhydrous distillate, several centigrams of alizarin are dissolved in a litre thereof, and 0·5 gram of dry tartaric acid in 10 c.c. The tartaric acid solution is then added slowly to the alcohol coloured by the

alizarin until the reddish-blue colour changes to a pure yellow; a few drops more of the tartaric acid solution are then added, and the whole distilled once more, care being taken to prevent the access of moisture. T. S. P.

True Homologues of Glycerol; Heptanetriol. J. L. HAMONET (*Compt. rend.*, 1916, **162**, 225—226).—A true homologue of glycerol is defined as a substance having the general formula $OH\cdot CH_2\cdot[CH_2]_n\cdot CH(OH)\cdot[CH_2]_n\cdot CH_2\cdot OH$, and an account is given of the preparation of *αδη-heptanetriol*, where $n=2$.

γ-Iodo-α-methoxypropane, $OMe\cdot CH_2\cdot CH_2\cdot CH_2I$, gives a magnesium derivative (compare A., 1904, i, 467), which, when acted on first by ethyl formate and then by water, yields *αη-dimethoxyheptan-δ-ol*, $OMe\cdot[CH_2]_3\cdot CH(OH)\cdot[CH_2]_3\cdot OMe$, b. p. 246—248°; D^{18} 0·969. This diether can be converted into heptanetriol by two methods. The first and longest consists in preparing by means of hydrobromic acid in the cold αγ-dibromoheptan-δ-ol, or in the hot αγδ-tribromoheptane; these yield respectively the corresponding diacetin and triacetin, which on saponification give the required heptanetriol. The bromo-compounds cannot be converted directly by the action of boiling water into the required glycerol, since under these conditions they yield propyltetrahydrofuran.

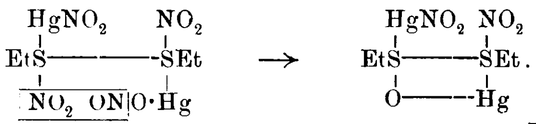
The second method consists in treating the αη-dimethoxyheptan-δ-ol, in the cold, with 2 mols. of anhydrous hydrogen iodide, the glycerol being dissolved out with water and obtained on distillation. *αδη-Heptanetriol*, $OH\cdot CH_2\cdot[CH_2]_2\cdot CH(OH)\cdot[CH_2]_2\cdot CH_2\cdot OH$, is a very viscous liquid, with a bitter taste, b. p. 230—232°/20 mm.; D^{18} 1·075. The method should apparently be general for the preparation of other homologues. W. G.

Mercury Mercaptide Nitrites and their Reactions with the Alkyl Iodides. Compounds of the Disulphonium Series. PRAFULLA CHANDRA RÂY (T., 1916, **109**, 131—138).—In a preliminary note (P., 1914, **30**, 140) it was shown that mercuric nitrite readily reacts with mercaptans to form mercury mercaptide nitrites of the type $R\cdot S\cdot HgNO_2$. The methyl and ethyl members of this series have now been more thoroughly examined, particularly with regard to the action of alkyl iodides on them. This reaction is found to proceed as represented by the scheme $2R\cdot S\cdot HgNO_2+2RI=R_2S_2+Hg_2I_2+2R\cdot NO_2$, but this is immediately complicated by other changes. Instead of mercurous iodide, the mercuric salt is formed, probably by the abstraction of iodine from some more of the alkyl iodide, but the most interesting result is the production of complex salts of the type $R_2S_2,HgI_2,R'I$. These are regarded as sulphonium salts, in which the two bivalent atoms in ethyl sulphide have become quadrivalent, thus: $SRR'I\cdot SRI\cdot HgI$.

Mercury methyl- and *ethyl-mercaptide nitrites* are obtained by adding dilute alcoholic solutions of the mercaptans to an excess of concentrated mercuric nitrite solution. Nitrous fumes are evolved, and the products separate as almost white, crystalline, nacreous precipitates.

The reaction with alkyl iodides is brought about by warming the mercury mercaptide nitrite with an excess of the iodide on the water-bath, until the mixture separates into two or three distinct layers. Besides volatile products, it is recognised that other complex substances are formed as well as the disulphonium compounds, but these are usually separated by fractional crystallisation from acetone. *Ethyldisulphonium-mercuri-iodide*, $SEt_2I{\cdot}SEtI{\cdot}HgI$, forms yellow crystals, m. p. 112°; the *compound*, Me_2S_2,HgI_2,EtI, from mercury methyl mercaptide nitrite and ethyl iodide, has m. p. 69—71°; the *compound*, Et_2S_2,HgI_2,PrI, from *n*-propyl iodide, forms dark brown, shining crystals, m. p. 75—78°; and the *compound*, Me_2S_2,HgI_2,PrI, is a yellow, mealy substance, m. p. 99—102°.

An alcoholic solution of ethyl disulphide also reacts with mercuric nitrite, nitrous fumes being evolved, and a *compound*, $Et_2S_2,Hg(NO_2)_2,HgO$, being precipitated in microscopic needles. The formation of the latter is interesting, as it throws some light on the constitution of the above complexes. It is assumed that the sulphur atoms first add mercuric nitrite and then nitrogen trioxide is eliminated, thus:



J. C. W.

Preparation of Ethyl Acetate from Acetaldehyde. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Eng. Pat., 1915, 1288; from *J. Soc. Chem. Ind.*, 1916, **35**, 141).—Ethyl acetate is produced in 85% yield when 400 parts of acetaldehyde are gradually stirred into a filtered solution of 16—20 parts of aluminium ethoxide in 45 parts of dry solvent naphtha, or other organic solvent of high boiling point, such as nitrobenzene or xylene, the temperature being maintained at 0—15° by thorough cooling. After keeping for twenty-four hours, the product is fractionally distilled, and the first runnings of acetaldehyde used again. Ethyl acetate forms the intermediate fraction, and from the residue the naphtha is recovered by steam distillation. G. F. M.

Preparation of Esters of Unsaturated Alcohols from Aldols. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1991—1993).—The action of magnesium amalgam on aldol yields the acetyl derivative of crotonyl alcohol: $OH{\cdot}CHMe{\cdot}CH_2{\cdot}CHO =$

$$2CH_3{\cdot}CHO. \quad OH{\cdot}CHMe{\cdot}CH_2{\cdot}CHO + CH_3{\cdot}CHO =$$
$$OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}OAc = H_2O + CHMe{:}CH{\cdot}CH_2{\cdot}OAc.$$

When treated with alumina, this ester is readily converted into erythrene and acetic acid (this vol., i, 4). If analogous and homologous aldols exhibit similar behaviour towards magnesium amalgam, this reaction would represent a new method for obtaining esters of unsaturated alcohols. T. H. P.

Hydrogenation of Oils. L. HAMBURGER (*Chem. Weekblad.*, 1916, **13**, 2—13).—An account of results obtained in the hydrogenation of oils by Sabatier's method under pressures up to 200 atmospheres. A. J. W.

Hardening of Oils in Presence of Nickel Borate. H. SCHÖNFELD (*Zeitsch. angew. Chem.*, 1916, **29**, 39—40).—The author disputes the statement of Bosshard and Fischli (A., 1915, ii, 788) that the catalytic hydrogenation of oils in presence of nickel borate is conditioned by the previous decomposition of the salt; the reverse, in fact, is the case, for with increasing decomposition of the borate owing to the action of the free oleic acid used in Bosshard's experiment the activity of the catalyst diminishes. The relatively high nickel content of the oleic acid hardened in presence of nickel borate is likewise to be attributed to the decomposition of the salt by the free fatty acid. G. F. M.

Oxidation of Δ^{α}-Hypogæic Acid by Alkaline Permanganate Solution and by Caro's Reagent. N. ZIMOVSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2121—2124).—Oxidation of Δ^{α}-hypogæic acid, m. p. 47—49°, solidifying point 44—43° (compare Ponzio, A., 1905, i, 405), by means of alkaline permanganate solution, yields an *αβ-dihydroxypalmitic acid*, $CO_2H\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_{12}\cdot CH_3$, which crystallises in needles, m. p. 125—127°, solidifying point 123—121°; 1·43 parts dissolve in 100 parts of alcohol at 19° and 0·15 part in 100 parts of ethyl ether at 18°.

Oxidation of Δ^{α}-hypogæic acid by means of Caro's reagent in the conditions employed by Albitzki (A., 1903, i, 288) yields a *dihydroxypalmitic acid*, $C_{16}H_{32}O_4$, m. p. 105—106·5°, solidifying point 102·5—100°; 7·94 parts dissolve in 100 parts of alcohol at 19°, and 1·39 parts in 100 parts of ether at 18°. T. H. P.

Oxidation of Δ^{ζ}-Oleic and Δ^{ζ}-Elaidic Acids by Alkaline Permanganate Solution and by Caro's Reagent. I. AFANASIEVSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2124—2127).—Oxidation of petroselic acid (compare Vongerichten and Köhler, A., 1909, i, 454) by means of Caro's reagent under the conditions indicated by Albitzki (A., 1903, i, 228) yields a *εζ-dihydroxystearic acid*, $CO_2H\cdot[CH_2]_4\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_{10}\cdot CH_3$, m. p. 96—99°, solidifying point 92—90°, which is stereoisomeric with the acid, m. p. 122°, obtained when the oxidation is effected by permanganate (Vongerichten and Köhler, *loc. cit.*). Oxidation of Δ^{ζ}-elaidic acid, m. p. 52—54°, by alkaline permanganate gives a dihydroxystearic acid, $C_{18}H_{36}O_4$, having the same melting point, 96—99°, as that described above. An isomeric acid, m. p. 120—123°, solidifying point 116—114°, is obtained by oxidising Δ^{ζ}-elaidic acid by means of Caro's reagent. T. H. P.

Glycerides of Linoleic Acid. AD. GRÜN and H. SCHÖNFELD (*Zeitsch. angew. Chem.*, 1916, **29**, 37—39).—*αα-Dilinolein* was obtained by the action of potassium linoleate on *αα*-dichlorohydrin,

and in better yield by the elimination of bromine by means of potassium iodide in ethyl acetoacetate solution from *αα*-di-tetrabromostearin, which was prepared in good yield by the action of potassium tetrabromostearate on *αα*-dichlorohydrin. *αα*-Dilinolein formed a clear oil of neutral reaction, and gave on bromination in carbon tetrachloride a small quantity of the above *di-tetrabromostearin*, m. p. 71°. From glyceryl tribromide and potassium linoleate only a poor yield of trilinolein was obtained. Mixed triglycerides could not be obtained by the usual methods, but linoleodistearin and linoleodipalmitin were successfully prepared from distearin and dipalmitin by esterification with linoleic anhydride according to the method of Grün and Schacht (A., 1907, i, 462). These mixed glycerides are more soluble in the various fat solvents, and have lower melting points than the saturated glycerides, and the symmetrical compounds are less fusible than the asymmetric. s-*Linoleodipalmitin* has m. p. 28—29°, as-*linoleodipalmitin*, m. p. 11·5—13°, s-*linoleodistearin*, m. p. 42° and 36°, and as-*linoleodistearin*, m. p. 34°. G. F. M.

Glutaconic Acid. I. P. E. VERKADE (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 981—992).—In this and in subsequent communications the author supports J. F. Thorpe's views on the constitution of glutaconic acid, with evidence chiefly of a physicochemical nature.

In the first place, it is shown that the glutaconic acid prepared by widely differing methods is always the same. These methods are reviewed, and it is pointed out that: (1) Conrad and Guthzeit's method, starting with ethyl sodiomalonate and chloroform, is the quickest, but costly; (2) von Pechmann and Blaise's method, starting with acetonedicarboxylic acid, is very good; Morgenstern and Zerner's method (A., 1910, i, 656), starting with dichlorohydrin and potassium cyanide, is the best for large-scale operations; and that Buchner's method, which involves as a preliminary the condensation of methyl acrylate with ethyl diazoacetate, results in the production of a mixture of glutaconic acid, and *cis*- and *trans*-trimethylenedicarboxylic acids, which can be separated by fractional crystallisation from water, ether, and ethyl acetate. The specimens of glutaconic acid obtained had m. p. 136—138°, and all had the usual properties.

The author emphasises the point that this ordinary form of glutaconic acid is superior in stability to the other two possible isomerides. It will be shown that it has neither all the properties of a *cis*-acid nor all those of a *trans*-acid, and that the speed at which it is reduced by hydrogen and a platinum catalyst is different from the rate at which an acid with a fixed double linking is reduced, and the course of the hydrolysis of the hydroxy-anhydride will be studied by physico-chemical means. All the evidence points to the presence of a "floating" double bond.

An attempt was made to effect a new synthesis of glutaconic acid by the hydrolysis of "ethyl *α*-cyanoglutaconate." This was prepared by condensing ethyl sodioformylacetate with ethyl cyanoacetate, but,

as Guthzeit and Eyssen have found (A., 1909, i, 674), it yields no glutaconic acid or pyridine derivatives on hydrolysis, which might have been expected from the hydrolysis of ethyl α-cyano-β-methylglutaconate (Thorpe and Rogerson, T., 1905, **87**, 1685). Probably, the ester has the structure:

$$CH\left\langle\begin{array}{l} C(CO_2Et)\cdot C{:}NH \\ \qquad\qquad\quad >O \\ CH{=\!=\!=}C\cdot OEt \end{array}\right. .$$

J. C. W.

Oxidation of Unsaturated Fatty Oils and Unsaturated Fatty Acids. I. Formation of Acraldehyde by the Oxidation of Linseed Oil and Linolenic Acid. ARTHUR HENRY SALWAY (T., 1916, **109**, 138—145).—A satisfactory explanation of the chemical processes involved in the "drying" of linseed oil would seem to be impossible until the oxidation of the constituent unsaturated glycerides is understood. Since it is extremely difficult to obtain the pure glycerides of linolenic, linoleic, and oleic acids, however, and since it can be shown that the glycerol plays no part in the reactions, the author has commenced a study of the action of air or oxygen on the free acids. He has shaken linseed oil, the mixture of acids from saponified linseed oil, linolenic acid, and oleic acids with oxygen in a bulbed tube immersed in water at 100°, and connected on the one hand to a manometer and gas cylinder, and on the other to a wash-bottle containing water, and he has found that, except in the case of oleic acid (and also pure glycerol), acraldehyde is one of the volatile products.

The literature of the subject is not very extensive, but contains references which are interesting in the light of the above. Thus, Dunlop and Shenk (*J. Amer. Chem. Soc.*, 1903, **25**, 826) noticed an odour of acraldehyde about "drying" linseed oil; Baly (A., 1912, i, 533) attributed the toxicity of the vapours of fresh paint to unsaturated aldehydes; and Gardner (A., 1914, i, 380) and King (A., 1915, i, 645) observed the production of carbon monoxide and carbon dioxide. An explanation of the mechanism of the processes, which would account for the formation of these substances, but, however, would involve a new conception of the structure of linolenic acid, is given, and the interesting suggestion is made that the "dry" oil contains the polymerides of acraldehyde and glyoxal.

J. C. W.

Composition of the Hydrochlorides obtained from Formaldoxime. C. H. SLUITER (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1007—1012).—Scholl (A., 1891, i, 663) stated that the composition of formaldoxime hydrochloride varies, owing to a progressive change which takes place during the formation of the salt, but Dunstan and Bossi (T., 1898, **73**, 353) assigned the definite formula $(CH_2{:}N\cdot OH)_3,HCl$, to the only substance which they could isolate in a pure state.

The author has reinvestigated these salts, and finds that Scholl's opinion was correct. The freshly prepared salt, crystallised once from methyl alcohol and then from ether, and dried in a current of dry hydrogen chloride, contains about 1 molecule of the acid to

1 of the simple oxime, $CH_2:N\cdot OH$; in a vacuum, this salt quickly changes into one containing 1HCl to $2CH_2:N\cdot OH$, and after repeated crystallisations and long drying, this gives Dunstan's salt, 1HCl to $3CH_2:N\cdot OH$. It is assumed, therefore, that the oxime molecule changes in structure, and the strength of the bases present at the various stages has been measured by their catalytic effect on the hydrolysis of ethyl acetate and sucrose. The facts are best explained by assuming a cyclic arrangement of three molecules of the oxime, and will be dealt with more fully in another paper (*Rec. trav. chim.*). J. C. W.

Some Properties of Starch Considered from a Colloid-Chemical Point of View. W. HARRISON (*J. Soc. Dyers*, 1916, **32**, 40—43).—Experiments are described which show that starch granules contain no starch which is really soluble in water, and that the outer portions of starch granules do not differ chemically from the inner portions. Such variations as are found in the starch granules are attributable to differences in the physical condition of the starch, the appearance of the granules under polarised light indicating a considerable degree of compression.

The differences in size, shape, and resistance to the action of hydrolytic agents which are shown by various kinds of starch granules are probably due to differences in the method and rapidity of deposition of the starch.

Observations on the precipitation of starch solutions by alcohol indicate that the precipitation is connected with the presence of inorganic salts. By the fractional separation of the mineral constituents of ordinary starch by means of alcohol, purer varieties of starch have been prepared. Solutions of such relatively pure starch are found to deposit granules in contact with the glass of the containing vessel, and it is suggested that this is due to the coagulating influence of salts dissolved from the glass.

The precipitation of starch by inorganic substances has also been examined. The results show that the coagulating powers of the metals depend on the valency as shown by the following series of relative numbers: hydrogen, 1; sodium, 1; barium, 4; magnesium, 4; aluminium, 16. The precipitating action of barium hydroxide has been supposed to be due to the formation of a definite compound; the author's experiments show that this is not the case, but that the composition of the precipitate varies with the concentration of the solution in accordance with the adsorption formula.

H. M. D.

Preparation of Diethylamine. WILLIAM EDWARD GARNER and DANIEL TYRER (T., 1916, **109**, 174—175).—A mixture of mono-, di-, and tri-ethylamine can easily be separated by fractionating with a 10-bulb column, and the authors have therefore been able to make diethylamine on a large scale in the laboratory, starting with ethyl bromide and ammonia. J. C. W.

Preparation of a Compound of Silver Glycocholate Readily Soluble in Water. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (U.S. Pat. 1161867; from *J. Soc. Chem. Ind.*, 1916, **35**, 141).—Hexamethylenetetramine–silver glycocholate is obtained as a colourless compound, soluble in water, in 90% alcohol, and in methyl alcohol, but almost insoluble in light petroleum, by treating silver glycocholate with a solution of hexamethylenetetramine. The aqueous solution of the compound is decomposed by hydrochloric acid into hexamethylenetetramine hydrochloride, silver chloride, and glycocholic acid. G. F. M.

Heptamethylenebis α-imino-acids and the Stereoisomerism of their Copper Salts. N. A. SCHLEZINGER (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1811—1819).—As is the case with the copper salts of other organic and inorganic acids, the copper salts of the majority of bisimino-acids are known only in one modification. The results obtained with the copper salts of αε-pentamethylenebisimino*iso*-butyric acid (A., 1915, i, 945) indicate that these salts are capable of exhibiting *cis-trans* isomerism, but only the less soluble isomeride could be isolated in the pure state. From the structural formulæ of the copper salts of αα-polymethylenebisimino-acids it is evident that the *cis*-salts should be the more stable when the number of methylene groups is small, and the *trans*-salts when more methylene groups are present. It is therefore clear why with αβ-ethylene- and αγ-trimethylenebisimino-acids the blue copper salt is alone observed, whilst only with the pentamethylene-acid does the second, violet form appear, although in this case also the blue form exhibits almost perfect stability. With the corresponding heptamethylene-acids, for instance, αη-heptamethylenedi-iminodi*iso*butyric acid, both copper salts are obtainable in the pure, crystalline, anhydrous condition; the stable, violet form exhibits normal molecular weight in freezing phenol, but no suitable solvent could be found for the labile blue modification.

*αη-Heptamethylenedi-iminodi*iso*butyronitrile*,

$$C_7H_{14}(NH\cdot CMe_2\cdot CN)_2,$$

prepared from heptamethylenediamine, potassium cyanide, and acetone, forms an almost colourless oil, and its *hydrochloride*, $+2HCl$, when rapidly heated in a sealed capillary, has m. p. about 129° (decomp.). The corresponding *acid*, $C_{15}H_{30}O_4N_2$, forms anhydrous crystals, and does not melt even at 310°. The violet-red *copper* salt, which is probably the *trans*-isomeride, is obtained by mixing the theoretical amount of cupric hydroxide with an ammoniacal solution of the acid and evaporating the solution. The blue *cis*(?)-modification is obtained by dissolving the violet salt in fused phenol, shaking the solution with much water to dissolve part of the phenol, and dissolving the rest of the latter in alcohol; the colour of this liquid gradually changes to blue, and extraction with ether then yields the blue salt; the latter is converted into the violet form slowly by boiling alcohol or rapidly by hot water, but the dry salt is not changed by prolonged heating at 90°.

αη-Heptamethylenedi-iminodiphenyldiacetonitrile,

$C_7H_{14}(NH\cdot CHPh\cdot CN)_2$,

prepared from heptamethylenediamine, potassium cyanide, and benzaldehyde, is an oil, and its *hydrochloride* has m. p. 144° (decomp.) in a sealed capillary. The corresponding *acid*, $C_{23}H_{30}O_4N_2$, decomposes at about 231° in a sealed capillary; its *hydrochloride*, $+H_2O$, was prepared, and its *methyl* ester, $C_{25}H_{34}O_4N_2$, forms a viscous oil, D_4^{20} 1·0854, n_D^{20} 1·5293; the *blue* copper salt was obtained as above. T. H. P.

Preparation of a Derivative of α-Bromo*iso*valeramide. KNOLL & Co. (D.R.-P. 287017; from *J. Soc. Chem. Ind.*, 1916, **35**, 142).—α-Bromo*iso*valeramide reacts with oxalyl chloride according to the equation:

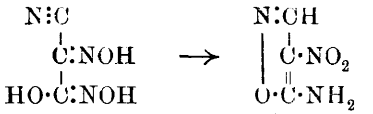
$$2NH_2\cdot CO\cdot CHBr\cdot CHMe_2 + C_2O_2Cl_2 = CO(NH\cdot CO\cdot CHBr\cdot CHMe_2)_2 + 2HCl + CO.$$

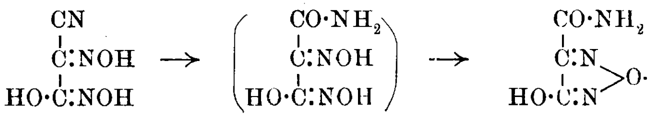
The derivative produced has sedative and hypnotic properties, and also serves as the starting point for the preparation of α-bromo-*iso*valerylcarbamide. G. F. M.

Preparation of Carbamide, and of Ammonium Carbonate for Use in its Preparation. BADISCHE ANILIN- & SODA-FABRIK. (Eng. Pat., 1914, 23939; from *J. Soc. Chem. Ind.*, 1916, **35**, 141).—Ammonium carbonate is prepared by the direct union of ammonia and carbon dioxide in suitable proportions under pressure, with or without cooling. The reaction is carried out in a lead- or silver-lined autoclave, and if instead of allowing the vessel to cool and the ammonium carbonate to solidify, it is only cooled sufficiently to keep the pressure below 50 atm. during the reaction, and subsequently the temperature is maintained at 130—140°, carbamide is formed. G. F. M.

Constitution of the Fulminuric Acids. VIII. Metafulminuric Acid. C. ULPIANI (*Gazzetta*, 1916, **46**, i, 1—48. Compare A., 1912, i, 611).—The work of Ehrenberg (A., 1884, 419; 1885, 1192), Scholvien (A., 1885, 39; 1886, 137), Nef (A., 1895, i, 9), Palazzo and Tamburello (A., 1907, i, 298), and Wieland and Hess (A., 1909, i, 369) is discussed. The author finds that the transformation of metafulminuric acid into oximinocyanoacetohydroxamic acid takes place, not only under the influence of alkali, but also spontaneously, and occupies a few hours or a few months according to the conditions; the change is greatly accelerated by heat or alkali. In a desiccator, oximinocyanoacetohydroxamic acid undergoes no further appreciable alteration, but under other conditions, for instance, in a closed, paraffined vessel or in an open vessel, it is transformed completely into *iso*fulminuric acid in a few weeks. Marked discrepancies occur between the properties found by the author for oximinocyanoacetohydroxamic acid and those ascribed to it by Nef and by Wieland and Hess, and the author shows that these are due to the fact that this acid undergoes change in different directions according to the conditions in which it is kept. (1) In solution in water or an organic solvent, it is trans-

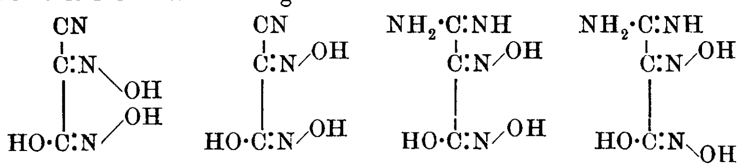
formed into an uncrystallisable syrup, the syrupy fulminuric acid of Ehrenberg, and this has not yet been purified, but is still under investigation. (2) When heated for about thirty minutes at 70°, the anhydrous form of oximinocyanoacetohydroxamic acid is converted into 4-nitro-5-amino*iso*oxazole (annexed formula) (A., 1912, i, 611). The transformation of the group $\cdot C(:NOH)\cdot C(:NOH)\cdot$ into $\cdot C(NO_2):C(NH_2)\cdot$ here taking place is in accord with the general law that a substance corresponding with a form of intermediate oxidation tends to decompose in two senses, namely, into the forms of lowest and highest oxidation. (3) The most typical change of oximinocyanoacetohydroxamic acid is, however, that into *iso*fulminuric acid or hydroxyfurazancarbonamide, which the author explains by the scheme:





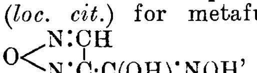
This reaction evidently requires the presence of only a minimal amount of moisture, but cannot take place in a desiccator.

To oximinocyanoacetohydroxamic acid (I) and the orange acid (II) obtained from it by the action of sodium hydroxide, and to the two amidines (III and IV) obtained by the action of dilute or concentrated ammonia solution on acid (I), the following stereoisomeric formulæ are assigned:

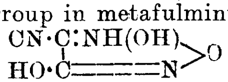


(I.) (*Syn.*) (II). (*Amphi.*) (III.) (White, *amphi.*) (IV.) (Yellow, *anti.*)

The author adopts the structure proposed by Wieland and Hess (*loc. cit.*) for metafulminuric acid. The furazanic formula,



is also discussed, in view of the fact that furazancarboxylic acid, when converted into its salts, undergoes transformation into oximinocyanoacetic acid; since, however, sodium nitrite acts rapidly on oximinocyanoacetohydroxamic acid, giving immediate and copious evolution of nitrous oxide and formation of oximinocyanoacetic acid, whereas with fulminuric acid this reaction takes place only with extreme slowness, the conclusion is drawn that the hydroxamic acid group in metafulminuric acid is not free, but bound. The structure

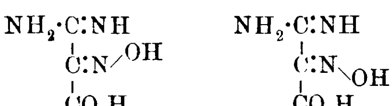


for metafulminuric acid is also considered.

Metafulminuric acid has m. p. 86° ($+2H_2O$) or 102° (anhydrous), the anhydrous form being non-explosive.

Oximinocyanoacetohydroxamic acid, $C_3H_3O_3N_3 + 3H_2O$, softens at about 45°, and is completely liquid at about 80°; with $\frac{1}{2}H_2O$ it has m. p. 105°. With ferric chloride its aqueous solution gives an intense reddish-violet coloration, which, unlike the colour given with metafulminuric acid, is stable on addition of a few drops of dilute hydrochloric acid. Its *acetyl* derivative, $C_5H_5O_4N_3 + H_2O$, m. p. about 99°, and *triacetyl* derivative, $C_9H_9O_6N_3$, m. p. 55—57°, were prepared.

The *mono-ammonium* salt of oximinocyanoacetohydroxamic acid, $C_3H_3O_3N_3,NH_3$, forms yellow needles, m. p. 115° (violent decomp.). The *diammonium* salt, $C_3H_3O_3N_3,2NH_3$, wrongly described by Scholvien (*loc. cit.*) as the diammonium salt of metafulminuric acid, forms microscopic crystals, m. p. 125° (decomp.). The corresponding amphi-*amidine* (*vide supra*), $C_3H_6O_3N_4$, obtained when an aqueous solution of either ammonium salt is left in an open vessel and described by Scholvien (*loc. cit.*) as the ammonium salt of metafulminuric acid, forms white crystals and begins to contract and turn brown at about 170°, becoming completely charred at 185°; the *nitrate*, m. p. 119—120°, and the *sulphate*, m. p. 153° (decomp.) were prepared. When converted into salts by treatment with mineral acids, the stable *amphi*-amidine is transformed into salts of the labile, yellow *syn*-modification, which undergoes spontaneous change into the *amphi*-form when suspended in water. The isomeric anti-*amidine*, obtained on gradual evaporation of a solution of the diammonium salt of oximinocyanoacetohydroxamic acid in concentrated ammonia solution, forms intensely yellow, slender needles; its *nitrate*, m. p. 120°, and *sulphate*, m. p. 145° (decomp.), were prepared.


(I.) (II.)

The action of sodium nitrate on salts of the above *anti*-amidine yields the *amidine* of *anti*-oximinocyanoacetic acid (annexed formula I), which forms microscopic needles charring at above 200°, and gives a faint, Marsala-yellow coloration with ferric chloride and an intense blue coloration with ferrous sulphate and a trace of potassium hydroxide or ammonia solution. The action of sodium nitrite on salts of the *syn*-amidine of oximinocyanoacetohydroxamic acid yields the amidine (I) just described, and also that of *syn*-oximinocyanoacetic acid (annexed formula II), which forms microscopic needles, carbonising at about 300°, and gives a Marsala coloration with ferric chloride and an intense blue coloration with ferrous sulphate mixed with either sodium acetate or potassium hydroxide or ammonia solution; the formation of the two isomeric amidines in this case is due to the spontaneous transformation in solution of the labile, yellow *syn*-amidine of oximinocyanoacetohydroxamic acid into the stable, white *amphi*-isomeride. By prolonged heating on the water-bath with dilute hydrochloric acid, the amidine of *anti*-oximinocyanoacetic acid is transformed into the

isomeric *syn*-compound. Reasons are given for regarding these two pairs of amidines as stereoisomerides and not structural isomerides (compare Wieland and Hess, *loc. cit.*).

In presence of 1 equivalent of sodium ethoxide, metafulminuric acid gives rise successively to the following monosodium salts of oximinocyanoacetohydroxamic acid: yellow, $C_3H_2O_3N_3Na$, red ($+1\frac{1}{2}H_2O$), and black ($+1\frac{1}{2}H_2O$), these corresponding respectively with the following modifications of the hydroxamic acid: white, crystalline; orange, insoluble; and green, which could not be separated from solution. The action of two equivalents of sodium ethoxide on either metafulminuric or oximinocyanoacetohydroxamic acid yields the amorphous, yellow disodium salt of the latter acid, $C_3HO_3N_3Na_2+3H_2O$, then the bright yellow disodium salt of the isomeric orange acid ($+2H_2O$), and, finally, the disodium salt of *iso*fulminuric acid. T. H. P.

Some Points Connected with the Representation of the Benzene Formula. GERVAISE LE BAS (*Chem. News*, 1916, **113**, 73—74).—The formula for benzene suggested in a previous paper (*ibid.*, 1914, **110**, 37) may be combined with the centric formula to yield a combination formula which is said to include the Kekulé formula. On the assumption of vibrating valencies and directive forces for positive and negative valencies, it is found that the centric formula may be regarded as a transition phase with the two alternative Kekulé formulæ as the limiting phases. H. M. D.

Preparation of 1 : 4-Dichloronaphthalene. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 286489; from *J. Soc. Chem. Ind.*, 1916, **35**, 107).—Dichloronaphthalenes, of which the 1:4-isomeride is the main product, are exclusively formed by the action of the calculated quantity of sulphuryl chloride on naphthalene at temperatures above 100°. They are used as intermediate products for the production of dyes. G. F. M.

Polymorphism in Halogen-substituted Anilides. FREDERICK DANIEL CHATTAWAY and GEORGE ROGER CLEMO (T., 1916, **109**, 89—105. Compare this vol., i, 140).—Some 2:4-dihalogenoacetanilides and -nitrobenzanilides have been obtained in two crystalline forms, and a large number of other derivatives of halogenoanilines have been prepared.

2:4-Dibromoaniline is conveniently obtained by heating aceto-*p*-bromoanilide with bromine in the presence of glacial acetic acid and sodium acetate, followed by hydrolysis. 2-Chloro-4-bromoaniline is obtained by the action of chlorine on aceto-*p*-bromoanilide, and 4-chloro-2-bromoaniline by heating aceto-*p*-chloroanilide with bromine, the products being subsequently hydrolysed.

Aceto-2-chloro-4-bromoanilide and aceto-4-chloro-2-bromoanilide crystallise from well-boiled solutions in glacial acetic acid, on cooling slowly, in tufts of slender needles, which sooner or later give place to compact crystals.

n-*Butyro-2-chloro-4-bromoanilide*, $C_6H_3ClBr\cdot NH\cdot CO\cdot C_3H_7$, forms

long, colourless needles, m. p. 110°, extinction 21°, and the -4-*chloro-2-bromoanilide* has m. p. 111·5°, extinction 31°. *Phenylaceto-2-chloro-4-bromoanilide*, $C_6H_3ClBr\cdot NH\cdot CO\cdot CH_2Ph$, forms colourless needles, m. p. 150°, extinction variable; the -4-*chloro-2-bromoanilide* has m. p. 148°; the -2:4-*dibromoanilide* has m. p. 160°. o-*Nitrobenzo-2-chloro-4-bromoanilide*,

$$C_6H_3ClBr\cdot NH\cdot CO\cdot C_6H_4\cdot NO_2,$$

forms colourless needles, m. p. 165°, extinction 25°; the -2:4-*dibromoanilide* crystallises in pale yellow plates, m. p. 178°, extinction 24°; the -4-*chloro-2-bromoanilide* forms colourless plates, m. p. 166°, extinction 18°; the -2:4-*dichloroanilide* has m. p. 153·5°. m-*Nitrobenzo-2-chloro-4-bromoanilide* separates in long needles, m. p. 191°; the -2:4-*dibromoanilide* has m. p. 165°, extinction variable; the -4-*chloro-2-bromoanilide* forms flattened plates, m. p. 167·5°, which show a small positive biaxial figure in convergent light; the -2:4-*dichloroanilide* has m. p. 183°, extinction straight. p-*Nitrobenzo-2-chloro-4-bromoanilide* separates when a concentrated alcoholic solution is rapidly cooled as a felt-like mass of almost colourless filaments, but these soon give place to pale yellow, hexagonal plates, m. p. 199°, extinction straight; the -2:4-*dibromoanilide*, m. p. 194°, crystallises in very similar forms; the -4-*chloro-2-bromoanilide* separates in very slender needles with straight extinction, which change slowly into pale yellow, stout, six-sided, rhombic plates, with diagonal extinction, m. p. 174°; the -2:4-*dichloroanilide* forms very slender needles, which change in the course of a few weeks into stout, six-sided prisms with domed ends, m. p. 174°.

The 2:4-dihalogenoanilines were also condensed with phthalic anhydride, at 180°. *Phthalo-2-chloro-4-bromoanil*,

$$C_6H_4{<}^{CO}_{CO}{>}N\cdot C_6H_3ClBr,$$

m. p. 165°, the -4-*chloro-2-bromoanil*, m. p. 140°, the -2:4-*dichloroanil*, m. p. 155°, and the -2:4-*dibromoanil*, m. p. 153·5°, all crystallise in colourless prisms with straight extinction.

The anilines were also treated with methyl or ethyl chloroformate in pyridine and ether. *Methyl 2-chloro-4-bromocarbanilate*, $C_6H_3ClBr\cdot NH\cdot CO_2Me$, forms colourless needles, m. p. 76·5°, extinction 42°; the *ethyl* ester has m. p. 96°, extinction 38°. Methyl and ethyl 2:4-dibromocarbanilates had already been obtained by less suitable means (Fromm and Heyder, A., 1909, i, 911). *Methyl 4-chloro-2-bromocarbanilate* has m. p. 87·5°, and the *ethyl* ester, m. p. 90°. *Methyl 2:4-dichlorocarbanilate* crystallises in needles, m. p. 70·5°, and the *ethyl* ester has m. p. 89°.

s-Bis-dihalogenophenylcarbamides were obtained by heating the anilines with an excess of carbamide at 180° for forty hours. s-2:2′-*Dichloro-4:4′-dibromodiphenylcarbamide*,

$$CO(NH\cdot C_6H_3ClBr)_2,$$

separates from nitrobenzene in hair-like needles with oblique extinction, m. p. 279°, whilst the very similar s-4:4′-*dichloro-2:2′-dibromodiphenylcarbamide* has m. p. 274° and extinction 40°.

The anilines were also heated with an excess of ethyl oxalate at 220°, when the oxanilates and small quantities of the oxanilides

were formed. The corresponding oxanilic acids and oxanilamides were prepared from the esters. *Ethyl* 2-*chloro*-4-*bromo-oxanilate* forms colourless needles, m. p. 124°; the free *acid*,

$$C_6H_3ClBr\cdot NH\cdot CO\cdot CO_2H,$$

has m. p. 131° (decomp.); s-2:2′-*dichloro*-4:4′-*dibromo-oxanilide* crystallises from nitrobenzene in colourless needles, m. p. 285°; 2-*chloro*-4-*bromo-oxanilamide*, $C_6H_3ClBr\cdot NH\cdot CO\cdot CO\cdot NH_2$, has m. p. 243°. *Ethyl* 4-*chloro*-2-*bromo-oxanilate* has m. p. 121°; the *acid* crystallises from benzene in colourless needles, m. p. 126—127° (decomp.) or from water with $1H_2O$; the *oxanilide*,

$$C_{14}H_8O_2N_2Cl_2Br_2,$$

has m. p. 295°; the *oxanilamide* has m. p. 236°. *Ethyl* 2:4-*dibromo-oxanilate* forms curved, hair-like crystals, m. p. 130°; the *acid* crystallises from benzene in needles, m. p. 138° (decomp.) and from water with $1H_2O$; 2:4:2′:4′-*tetrabromo-oxanilide* has m. p. 298°, straight extinction; and the *oxanilamide* has m. p. 250°.

Similar compounds were obtained from ethyl malonate (compare T., 1910, **97**, 339). 2:2′-*Dichloro*-4:4′-*dibromomalonanilide*, $CH_2(CO\cdot NH\cdot C_6H_3ClBr)_2$, forms colourless needles, with straight extinction, m. p. 214°. *Ethyl* 2-*chloro*-4-*bromomalonanilate*, $C_6H_3ClBr\cdot NH\cdot CO\cdot CH_2\cdot CO_2Et$, crystallises in colourless, prismatic plates, with straight extinction, m. p. 81·5°; the free *acid* forms long, slender prisms, which melt and change into aceto-2-chloro-4-bromoanilide at 165°; the *amide*, $C_6H_3ClBr\cdot NH\cdot CO\cdot CH_2\cdot CO\cdot NH_2$, has m. p. 149°. 4:4′-*Dichloro*-2:2′-*dibromomalonanilide* crystallises in colourless prisms, m. p. 221°, straight extinction. *Ethyl* 4-*chloro*-2-*bromomalonanilate* separates from alcohol in prismatic plates, m. p. 83·5°; the *acid* forms long prisms, m. p. 161° (changing into aceto-4-chloro-2-bromoanilide; the *amide* crystallises in long, slender needles, m. p. 159°. 2:4-*Dibromomalonanilamide* forms slender needles, m. p. 164°.

Various sulphonanilides were obtained by adding an ethereal solution of the sulphonyl chloride to a solution of the aniline and pyridine in ether, and these were converted into *N*-chlorides by means of hypochlorous acid. *Benzenesulphon*-2-*chloro*-4-*bromo-anilide*, $C_6H_3ClBr\cdot NH\cdot SO_2Ph$, forms striated, colourless, flat prisms, with straight extinction, m. p. 122°, and *benzenesulphon*-2-*chloro*-4-*bromophenylchloroamide*, $C_6H_3ClBr\cdot NCl\cdot SO_2Ph$, crystallises in stout prisms, m. p. 111—112°. *Benzenesulphon*-4-*chloro*-2-*bromo-anilide* crystallises in flat prisms, terminated by domes with straight extinction, m. p. 128°, and the -*phenylchloroamide* forms stout prisms, m. p. 123°. p-*Toluenesulphon*-2-*chloro*-4-*bromoanilide*, $C_6H_3ClBr\cdot NH\cdot SO_2\cdot C_6H_4Me$, forms colourless plates, m. p. 121°, and the -*phenylchloroamide* separates from chloroform in stout prisms, m. p. 78°. p-*Toluenesulphon*-2:4-*dibromoanilide* crystallises in plates with straight extinctions, m. p. 134°, and the -*phenylchloro-amide* in stout prisms, m. p. 78°. p-*Toluenesulphon*-4-*chloro*-2-*bromoanilide* forms plates, m. p. 126·5°, and the -*phenylchloroamide* stout prisms, m. p. 77°. p-*Nitrotoluene*-o-*sulphon*-2-*chloro*-4-*bromo-anilide*, $C_6H_3ClBr\cdot NH\cdot SO_2\cdot C_6H_3Me\cdot NO_2$, crystallises in very pale yellow, obliquely terminated prisms, extinction 25°, m. p. 164·5°,

and the *-phenylchloroamide* in prisms, m. p. 123—124°. p-*Nitrotoluene-o-sulphon-4-chloro-2-bromoanilide* forms very pale yellow, flattened prisms, straight extinction, m. p. 165°, and the *-phenylchloroamide* colourless prisms, m. p. 122°. p-*Nitrotoluene-o-sulphon-2:4-dibromoanilide* crystallises in flat prisms with straight extinction, m. p. 173°, and the *-phenylchloroamide* in colourless prisms, m. p. 124—125°.

Azo-dyes with β-naphthol were found to be characteristic derivatives of the several anilines. *2-Chloro-4-bromobenzeneazo-β-naphthol*, $C_6H_3ClBr\cdot N_2\cdot C_{10}H_6\cdot OH$, crystallises in plates, m. p. 210°, which have a beetle-green colour by reflected light and a red colour by transmitted light. *4-Chloro-2-bromobenzeneazo-β-naphthol* forms brilliant, sharply pleochroic, red plates, with straight extinction, m. p. 193°. 2:4-Dibromobenzeneazo-β-naphthol (compare Hantzsch and Schmiedel, A., 1897, i, 185) forms flat, brick-red prisms, m. p. 203°, with straight extinction. J. C. W.

Imino-acids. G. L. Stadnikov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1792—1796).—The author replies to Schlezinger's criticisms (A., 1915, i, 959) of his views concerning the increasing instability of imino-acids with increase of the molecular weight. Against Schlezinger's conclusions the following facts are cited: (1) the nitrilo-ester of iminophenyldiacetic acid does not decompose at the imino-group when boiled with 20% hydrochloric acid, and thus resembles nitriles of the lower, aliphatic imino-acids; (2) under the same conditions, the nitrilo-ester of phenylmethyliminodiacetic acid partly decomposes at the imino-group, and thus occupies an intermediate position; and (3) the nitrilo-ester of *cyclo*heptaneiminopropionic acid is readily resolved at the imino-group by 20% hydrochloric acid. Schlezinger's views are also inapplicable to the case of the aliphatic imino-acid obtained by Erlenmeyer and Sigel (A., 1874, 981) from heptaldehyde–ammonia, the nitrile of this acid being decomposed at the imino-group by 20% hydrochloric acid. These and other observations are regarded as confirmation of the view that the stability of derivatives of imino-acids diminishes as the molecular weight increases, although the author does not deny the influence exerted by acidifying groups in organic compounds in general and in imino-acids in particular. Various instances are quoted to show that the same rule holds for the imino-acids themselves. T. H. P.

Reaction of Esters with Organo-magnesium Compounds. II. G. L. Stadnikov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2037—2044. Compare A., 1914, i, 954).—Further complications are encountered in the interaction of esters and organo-magnesium compounds when heavy radicles take part in the reaction (compare A., 1915, i, 957, 975). When a methyl or ethyl ester is used, the iodomagnesium *sec.*- or *tert.*-alkyloxide formed reacts with the unchanged initial ester, giving an ester corresponding with the alcohol synthesised. In some cases this ester will react with magnesium iodide, giving the iodide corresponding with the alcohol synthesised.

This iodide may then: (1) react with the iodomagnesium alkyloxide of the alcohol synthesised, giving the simple ether of such alcohol; (2) react with the iodomagnesium methoxide (or ethoxide) present, forming a mixed ether of the synthesised alcohol; (3) react with magnesium alkyl iodide, yielding a hydrocarbon (tri- or tetra-alkylmethane). Two conditions absolutely necessary for the reaction to proceed in the above directions are a high temperature and the presence of a sufficient proportion of the initial ester. The conditions employed were as follows: to the organo-magnesium compound, cooled by means of tap-water, the ester is added as far as possible at one time, and not in small portions; if the mixture begins to boil, the vessel is kept in water until the boiling is allayed, and is then heated on a bath to the boiling point of the ether for six to ten hours.

Under conditions such as these, magnesium phenyl bromide and methyl benzoate yield considerable proportions of triphenylmethyl methyl ether and triphenylcarbinol. With magnesium phenyl bromide and benzyl benzoate, a relatively small yield of triphenylmethyl benzyl ether is obtained, the reaction virtually stopping at the first stage, namely, the formation of iodomagnesium *tert.*-alkyloxide.

T. H. P.

Reaction of Esters with Organo-magnesium Compounds. III. G. L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2115—2120. Compare preceding abstract).—In those cases where the *tert.*-alkyl bromide or iodide, in presence of haloidomagnesium alkyloxide, gives an unsaturated hydrocarbon (A., 1914, i, 954), the whole cycle of reactions between an ester and a magnesium alkyl haloid is expressed by the following equations: (1) $CH_2R{\cdot}CO_2Et + 2MgR'X = CH_2R{\cdot}CR_2'{\cdot}O{\cdot}MgX + OEt{\cdot}MgX$; (2) $CH_2R{\cdot}CO_2Et + CH_2R{\cdot}CR'_2{\cdot}O{\cdot}MgX = OEt{\cdot}MgX + CH_2R{\cdot}CO_2{\cdot}CR_2'{\cdot}CH_2R$; (3) $CH_2R{\cdot}CO_2{\cdot}CR_2'{\cdot}CH_2R + MgI_2 = CH_2R{\cdot}CO_2{\cdot}MgI + CH_2R{\cdot}CR_2'I$; (4) $CH_2R{\cdot}CR'_2I + OEt{\cdot}MgX = Et{\cdot}OH + MgXI + CR'_2{:}CHR$. The results obtained under different conditions are as follows: (*a*) If the ethyl ester acts on the magnesium alkyl haloid in the cold, and the ester is added in drops and the mixture energetically shaken meanwhile, the tertiary alcohol is obtained. (*b*) If the whole of the ester, taken in excess, is introduced at once into the solution of the magnesium alkyl haloid and the reacting mixture is then heated at the boiling point, the ethylenic hydrocarbon corresponding with the tertiary alcohol is obtained. (*c*) If the conditions are as under (*b*), but a benzyl ester is used, both the tertiary alcohol and the corresponding ethylenic hydrocarbon are obtained; thus, from benzyl acetate and magnesium phenyl bromide under these conditions, diphenylmethylcarbinol and *as.*-diphenylethylene are formed.

T. H. P.

Combination of Hydrogen with Acetylene Derivatives. VI. Hydrogenation of an Acetylenic Alcohol. J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2045—2050. Compare A., 1915, i, 640).—At the ordinary temperature, the hydrogenation of

δ-phenyl-β-methyl-Δ^{γ}-butinen-β-ol, $OH\cdot CMe_2\cdot C⋮CPh$ (compare Iocitsch, A., 1914, i, 401) in anhydrous alcoholic solution and in presence of colloidal palladium proceeds uninterruptedly, no arrest occurring when two atoms of hydrogen have been taken up per molecule of the alcohol.

β-Phenylethyldimethylcarbinol, $CH_2Ph\cdot CH_2\cdot CMe_2\cdot OH$, obtained in the above reaction, is a viscous liquid with a pleasant smell, b. p. 144°/85 mm., D_4^0 0·9778, $D_4^{20\cdot7}$ 0·9626, $n_D^{20\cdot7}$ 1·50775. Its *acetyl* derivative, $C_{13}H_{18}O_2$, is a colourless, viscous liquid, b. p. 131°/17 mm., D_4^0 0·9987, $D_4^{20\cdot7}$ 0·9831, $n_D^{20\cdot7}$ 1·48820. T. H. P.

Cholesterol and Coprosterol. III. The Ozonides of Cholesterol. IV. Action of Bromine on Cholesteryl Benzoate. CHARLES DORÉE and LIONEL ORANGE (T., 1916, **109**, 46—55).—The application of ozone to the determination of ethylene linkings in cholesterol and its derivatives has given very different results in the hands of various workers. Many of the pitfalls have now been recognised. Not only is it important, when aiming at a pure ozonide, to use pure ozone, washed free from oxozone, but chloroform must be abandoned as a solvent, and a weak ozone of only 1—2% concentration should be employed. The authors have therefore treated cholesterol and the acid, $C_{27}H_{44}O_4$ (Diels, A., 1903, i, 819) with pure and "crude" ozone in glacial acetic acid or acetone, and have purified the products by frequent precipitation by light petroleum from ethereal solutions, followed by exposure to a high vacuum for some days. They find that cholesterol combines with a maximum of six atoms of oxygen when treated with pure ozone, whilst seven atoms are absorbed when "crude" ozone is used, whereas the acid combines with 7 and 8 atoms respectively. The first stage, defined roughly as the point at which the cholesterol dissolves as an ozonide, suggests the formation of an ozonide, $+O_3$, with washed ozone, but the addition of O_4 with the crude ozone. All the products were brittle solids, m. p. 85—95°, decomp. above 100°, which were dextrorotatory and gave resinous acids and neutral substances on decomposition. The authors believe that the second unsaturated linking which is involved in the reaction is not pre-existent, but is developed by the breaking down of a bridged ring system.

Cholesterol was also heated with sulphur for several hours at 160—165°, at which point the element is supposed to exist as active S_3 molecules, analogous to ozone (Erdmann, A., 1908, ii, 830). A dark red, brittle solid was isolated, which is probably a "*monothio-ozonide*," $C_{27}H_{46}OS_3$.

Cholesteryl benzoate and nitrobenzoates behave towards bromine in a somewhat different manner from the other esters. In cold carbon disulphide solution no reaction seems to take place until a few minutes have elapsed, but then substitution, and also addition, set in rapidly. Bromocholesteryl benzoate, narrow, six-sided prisms, m. p. 140—142° (compare Obermüller, A., 1891, 299) and *cholesteryl benzoate dibromide*, $C_{34}H_{50}O_2Br_2$, large, hexagonal tablets, m. p. 168—169°, were isolated in the case of the benzoate. *Chole-*

steryl m-*nitrobenzoate*, m. p. 137° (turbid, clear at 170°) and the p-*nitrobenzoate*, glistening plates, m. p. 185° (turbid, clear at 250°), show a characteristic play of colours, violet, green, and red, on cooling. *Bromocholesteryl* m-*nitrobenzoate* crystallises in leaflets, m. p. 149°. J. C. W.

Mechanism of Perkin's Reaction. M. BAKUNIN and G. FISCEMAN (*Gazzetta*, 1916, **46**, i, 77—103).—The authors have made a number of experiments with the object of elucidating the behaviour of the various types of compounds characterising Perkin's synthesis. Between sodium acetate and phenylacetic anhydride or between sodium phenylacetate and acetic anhydride, a reversible reaction takes place:

$$2CH_2Ph\cdot CO_2Na + (CH_3\cdot CO)_2O \rightleftarrows 2CH_3\cdot CO_2Na + (CH_2Ph\cdot CO)_2O,$$

such a reaction also occurring when the radicles of the anhydride and salt are identical. Acetic anhydride alone does not react with aldehydes, except that with *p*-nitrobenzaldehyde it yields a little *p*-nitrocinnamic acid, reaction in general being determined by the presence of acetate. Phenylacetic anhydride is decidedly more reactive, and with aldehydes forms unsaturated acids, but the percentage yields of the latter are greatly increased by addition of sodium acetate or, to a less extent, sodium phenylacetate. The sole purpose of increasing the yield is served by adding acetic anhydride, which is a dehydrating agent capable of dissolving salts, anhydrides, and aldehydes, and therefore of rendering possible the intimate contact otherwise unattainable. It is advantageous, but not indispensable, that one of the compounds taking part in the double decomposition should be an anhydride, unsaturated acids being also obtained if the anhydride is replaced by an acid. The question of the formation of intermediate compounds in the reaction is discussed. T. H. P.

Derivatives of Cinnamic Acid: Syntheses of β-Phenyl-α-ethylcinnamic and β-Hydroxy-ββ-diphenyl-α-ethylpropionic Acid. R. DE FAZI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 92—99). —*β-Hydroxy-ββ-diphenyl-α-ethylpropionic acid*,

$$OH\cdot CPh_2\cdot CHEt\cdot CO_2H,$$

obtained from the corresponding ethyl ester (A., 1915, i, 1063), forms slender, white needles, m. p. 179—180°, and gives an emerald-green coloration with cold concentrated sulphuric acid, which converts it into 3-phenyl-2-ethylindone.

Ethyl β-phenyl-α-ethylcinnamate, $CPh_2{:}CEt\cdot CO_2Et$, prepared by the action of phosphoric oxide on ethyl β-hydroxy-ββ-diphenyl-α-ethylpropionate, forms large, shining, colourless prisms, m. p. 88—89°, and gives an emerald-green coloration with cold concentrated sulphuric acid, which converts it into 3-phenyl-2-ethylindone. The corresponding *acid*, $CPh_2{:}CEt\cdot CO_2H$, forms slender, white needles, m. p. 159—160°, and behaves like its ester towards sulphuric acid.

ββ-Diphenyl-α-ethylpropionic acid, $CHPh_2 \cdot CHEt \cdot CO_2H$, obtained by reducing the preceding acid by means of sodium amalgam, forms slender, white needles, m. p. 167—168°, and gives no coloration in the cold with concentrated sulphuric acid.

Ethyl β-phenyl-α-methylcinnamate, $CPh_2 \colon CMe \cdot CO_2Et$, prepared by the action of phosphoric oxide on ethyl β-hydroxy-ββ-diphenyl-α-methylpropionate, forms shining, colourless prisms, m. p. 87—88°, and gives in the cold an emerald-green coloration with concentrated sulphuric acid, which converts it into 3-phenyl-2-methylindone. The corresponding acid was prepared by Rupe, Steiger, and Fiedler (A., 1914, i, 281).

ββ-Diphenyl-α-methylpropionic acid, $CHPh_2 \cdot CHMe \cdot CO_2H$, forms slender, white needles, m. p. 164—165°, and gives no coloration with concentrated sulphuric acid. T. H. P.

Electrolysis of Organic Acids: Phenylpropiolic Acid. B. L. Vanzetti (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 533—536).—The electrolysis of phenylpropiolic acid has been investigated in order to ascertain whether the marked facility for decomposition shown by acetylenedicarboxylic acid (A., 1915, i, 494), evidently due to the presence of the triple linking, is repeated in the simplest acetylenic acid of the aromatic series; 28% solutions of potassium phenylpropiolate were electrolysed at various temperatures and under various current densities. The products consist of hydrogen, oxygen, and increasing proportions of carbon dioxide at temperatures above 50°, but in no case was the formation of carbon monoxide observed. No acetylene was formed, but minute proportions of unsaturated compounds were obtained at temperatures above 70°. During the first hours of the electrolysis, a pronounced odour of acetophenone is noticed, probably as the result of a reaction analogous to that occurring when phenylpropiolic acid is heated with water at 120°, $CPh \colon C \cdot CO_2H \longrightarrow CPh \colon CH \longrightarrow Ph \cdot COMe$.

Notwithstanding the presence of the triple linking, phenylpropiolic acid presents, therefore, considerable stability towards electrolysis, and thus bears a marked resemblance to benzoic acid, with which it has many other properties in common. T. H. P.

Bismuth Acetylsalicylate [*o*-Acetoxybenzoate]. L. Vanino and Fr. Mussgnug (*Arch. Pharm.*, 1916, **253**, 511—512).—Bismuth *o*-acetoxybenzoate is precipitated when a concentrated aqueous solution of bismuth nitrate (16 grams) and mannitol (6 grams) is added to a solution of sodium *o*-acetoxybenzoate (20 grams). Its physiological action is not different from that of known *o*-acetoxybenzoates. C. S.

Saponification of Benzoylated Cyanohydrins by Acetic Acid in Presence of Metallic Salts. J. Aloy and Ch. Rabaut (*Bull. Soc. chim.*, 1916, [iv], **19**, 44—46).—The benzoylated cyanohydrins of the aldehydes and ketones already described (compare A., 1913, i, 620, 728) can be readily hydrolysed by gently boiling 4 grams of the cyanohydrin with 25 c.c. of acetic acid (4 vols. of the glacial

acid to 1 vol. of water) and 1 gram of zinc oxide for two hours, and then pouring the liquid into water, when the corresponding amide separates and can be purified by crystallisation. In place of the oxide, the metal or its acetate can be used, and the amount of oxide used can be reduced if the duration of boiling is lengthened. The oxide of zinc can be replaced by the oxides of mercury, silver, nickel, cobalt, and copper, but hydrolysis does not occur in the presence of the oxides of lead, cadmium, aluminium, iron, chromium, thorium, or of the alkali or alkaline-earth metals. Manganese oxide exerts a slight, favourable action. The sulphates of zinc and copper also give good yields, but cobalt chloride is without action.

The benzoylated cyanohydrin from anisaldehyde yields the *amide*, $OMe \cdot C_6H_4 \cdot CH(OBz) \cdot CO \cdot NH_2$, m. p. 155°. W. G.

Preparation of Hydroxytriphenylmethanecarboxylic Acids. FARBENFABRIK VORM. F. BAYER & Co. (D.R.-P. 286744; from *J. Soc. Chem. Ind.*, 1916, **35**, 107).—Carboxyl groups are introduced into hydroxytriphenylmethanes by the action of carbon dioxide in the usual manner. The products such as 2-chloro-4′ : 4″-dihydroxy-3′ : 3″-dimethyltriphenylmethane-5′ : 5″-dicarboxylic acid and 4′ : 4″-bisdimethylamino-3-hydroxytriphenylmethane-4-carboxylic acid are used in the preparation of dyes. G. F. M.

Lichens and their Characteristic Constituents. XIII. O. HESSE (*J. pr. Chem.*, 1915, [ii], **92**, 425—466. Compare A., 1911, i, 208).—The inactive erythritol which has been noted in many *Rocellas* has recently received the correct designation, "meso-erythritol." The author suggests that the old name should be retained, however, and that the *d*- and *l*- and *dl*-isomerides should receive the systematic name "tetritol." The occurrence of erythritol or erythrin has been noted in two algæ, *Protococcus vulgaris* and *Chroolepus* (*Trentepohlia*) *Jolithus*, and also in the fungus *Ustilago Maidis*, so that their production in nature is not peculiar to lichens.

Aspicilia calcarea (*L.*) *Kbr.* (var. *farinosa*) collected in the rock gardens at Besigheim (Württ.) contained 0·11% erythrin and 0·23% erythritol.

Evernia prunastri (*L.*) contains atranorin and evernic acid when grown on birch, limes, beech, or sand-stone, but usnic acid, in addition, when found on oak. The following derivatives of evernic acid are described: potassium, *sodium*, *barium*, *calcium*, *copper*, *lead* and *silver* salts, and *diacetyl* derivative, $C_{17}H_{16}O_7Ac_2$, a crystalline powder, m. p. 144°. The evernic acid from this lichen has also been converted into everninic acid, and this has been identified with the acid synthesised by Fischer and Hoesch (A., 1912, i, 860). The following derivatives of everninic acid have been prepared: *acetyleverninic acid*, $C_9H_9O_4Ac$, colourless, short prisms, m. p. 111°; *nitroeverninic acid*, small, orange-red needles, m. p. 195°; *dinitroeverninic acid*, $C_9H_8O_4(NO_2)_2,H_2O$, golden-yellow needles, m. p. 87° (*potassium* salt, very explosive, yellow needles).

A well-developed form of *Evernia furfuracea* (*L.*) (var. *isidiophora*) was said by Zopf (1903) to contain "isidic acid." Some of

this lichen has been collected from birches and found to contain atranorin, evernuric acid, and physodylic acid, which agreed with Zopf's description of "isidic acid."

It is again found that *Parmelia caperata* (*L.*) when growing on limes, rocks, or walls contains *d*-usnic, caprarić, and caperatic acids, whilst specimens collected from oaks contained caperin and caperidin in addition.

Solorina crocea (*L.*) *Ach.*, collected in the Engadine district, has been extracted in the usual way with ether and then acetone, and solorinic and soloric acids, and hydrosolorinol isolated from the former extract and mannitol (1%) from the latter. Zopf (A., 1909, i, 238) found solorinic acid and mannitol, and a trace of "solorinin," which the author thinks might have contained soloric acid. Solorinic acid, $C_{23}H_{19}O_7{\cdot}OMe$, forms microscopic, red leaflets, and yields an acetyl derivative, $C_{24}H_{18}O_8Ac_4$ (*ibid.*), and a *benzoyl* derivative, $C_{24}H_{21}O_8Bz$, yellowish-brown needles, m. p. 153°. The yellowish-red solutions of the acid in acetic acid become pale on treatment with zinc dust, and *solorinol*, $C_{24}H_{24}O_7$, may then be isolated, as a brownish-yellow, crystalline powder, m. p. 162°. When boiled with hydriodic acid, it not only loses methoxyl, but is degraded to a much simpler compound, *solorol*, $C_{15}H_{14}O_7$, which forms yellowish-brown, microscopic leaflets, m. p. 216°. This substance yields a *hepta-acetate*, yellowish-brown needles, m. p. 215°, which may be oxidised by chromic acid to "*hexa-acetylsoloron*," $C_{15}H_6O_8Ac_6$, well-developed, yellowish-brown needles, m. p. 197°. "*Soloron*," $C_{15}H_{12}O_8$, forms scarlet needles, m. p. 280°, like rhodocladonic acid. *Hydrosolorinol*, $C_{24}H_{32}O_7$, occurs especially in the apothecia of the lichen, and it is best to pick these off separately in order to isolate the compound. It forms a dark violet, almost black, crystalline powder. *Soloric acid*, $C_{36}H_{36}O_{14}$, crystallises in colourless, soft needles, m. p. 205°, yields methyl betorcinolcarboxylate on methylation (A., 1898, i, 534), and is a homologue of gyrophoric acid.

Cladonia macilenta (*Ehrh.*) *Hoffm.* contains coccellic acid (0·4%) and thamnolic acid (0·1%) in the podetia and rhodocladonic acid in the apothecia. The latter acid may be reduced by adding zinc dust to a hot solution in glacial acetic acid, the product being *hydrorhodocladonic acid*, $C_{15}H_{14}O_8$, a bluish-black, crystalline powder.

Cladonia tenuis, *Floerke*, contains fumarprotocetraric acid and *d*-usnic acid, m. p. 196°, $[\alpha]_D^{16}$ + 494·1°.

Cladonia fimbriata (*L.*) var. *cornuto-radiata* was said by Zopf to contain fumarprotocetraric acid, but this cannot be confirmed. It probably contains nemoxynic acid, which Zopf first found in *C. nemoxyna* (*Chem. Zentr.*, 1908, ii, 2183).

Cladonia crispata (*Ach.*) var. *gracilescens* (*Rabenhorst*) is found to contain squamatic acid (Zopf, A., 1907, i, 219) and *cladonin*, $C_{30}H_{48}O_5$, a white, granular powder, m. p. 228°.

Cladonia condensata (*Floerke*) *Zopf* contains *l*-usnic acid (0·5%), $[\alpha]_D^{15}$ − 494·3°, and *cornicularin*, $C_{23}H_{44}O_5$, which forms microscopic granules, m. p. 229—230°.

Pycnothelia papillaria (*Dufour*) var. *molariformis* (*Hoffm.*)

[*Cladonia papillaria* (*Ehrh.*) var. *molariformis* (*Hoffm.*)] is found to contain atranorin (0·04%), cladonin, and proto-α-lichestearic acid, satin-like leaflets, m. p. 113—114°, $[\alpha]_D^{15}$ +22·3° (alcohol), 23·9° (chloroform).

Cornicularia aculeata, var. *stuppea Fw.*, has been examined again (*loc. cit.*). The constituent cornicularin, $C_{28}H_{44}O_5$, when pure, does not give a colour with ferric chloride, as was first supposed.

The sweet substance, $C_{12}H_{26}O_{11}$, previously reported in *Cornicularia aculeata*, var. *acanthella Ach.*, has crystallised in the course of time, and is recognised as dimannitol. It forms long, colourless needles.

Pertusaria ocellata variolosa, *Fw.*, contains atranorin and gyrophoric acid, which, according to an ebullioscopic determination of the molecular weight, has the formula $C_{32}H_{28}O_{14}$. J. C. W.

Preparation of *o*-Aldehydophenylglycine. W. GLUUD (D.R.-P. 286761; from *J. Soc. Chem. Ind.*, 1916, **35**, 106).—*o*-Aldehydophenylglycine may be obtained as the bisulphite compound by decomposing the corresponding oxime with sulphurous acid or its salts. The method is also applicable to derivatives of the oxime in which the carboxyl, oximino-, or imino-group is substituted. G. F. M.

Preparation of Condensation Products of *o*-Aldehydophenylglycine Oxime and its Derivatives Substituted in the Carboxyl Group. W. GLUUD (D.R.-P. 286762; from *J. Soc. Chem. Ind.*, 1916, **35**, 106).—The oxime or its derivative is treated for a short time at a high temperature with an aldehyde under such conditions that the oximino-group is not removed. Thus with formaldehyde the reaction is apparently as follows:

$$C_6H_4\left<\begin{matrix}CH:N\cdot OH\\ NH\cdot CH_2\cdot CO\cdot NH_2\end{matrix}\right. \xrightarrow{HCHO} C_6H_4\left<\begin{matrix}CH:N\text{———————}O\\ N(CH_2\cdot CO\cdot NH_2)\end{matrix}\right>CH_2 \xrightarrow{NaOH}$$

$$C_6H_4\left<\begin{matrix}CH:N\text{—————}O\\ N(CH_2\cdot CO_2H)\end{matrix}\right>CH_2.$$

The products are intended for dyes, medicinal preparations, and starting materials for the preparation of indoles. G. F. M.

Additive Molecular Compounds in Organic Chemistry. MICHELE GIUA (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 99—105).—The author discusses briefly the relations of complex inorganic compounds, intermetallic compounds, and organic, additive, molecular compounds to the theory of valency. Cryoscopic investigation of the system 2:4:6-trinitrotoluene–*p*-aminophenyl methyl ketone indicates the formation of the *compound*,

$$C_6H_2Me(NO_2)_3,NH_2\cdot C_6H_4\cdot COMe,$$

which forms shining, red prisms, m. p. 94°, and gives a garnet-red coloration with acetone and ammonia. The eutectic between

trinitrotoluene and this compound melts at 73°, and that between the compound and the amino-ketone at 85°. Picric acid and *p*-aminophenyl methyl ketone form the compound,

$$C_6H_2(NO_2)_3{\cdot}OH,C_8H_9ON,$$

which forms yellow needles, m. p. 130—131°. T. H. P.

3-Allylmenthanol, 3-Allyl-Δ^3-menthene and 1-Methyl-3-allyl-Δ^3-*cyclo*hexene. M. ZAJCEV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2127—2129. Compare A., 1913, i, 1370).—When treated with allyl iodide and zinc, (1) *l*-menthone, $[\alpha]_D$ $-27{\cdot}46°$, obtained by the oxidation of menthol, yields 3-*allylmenthanol*, b. p. 125—129°/18 mm., D_4^{20} 0·9058, $[\alpha]_D$ $-3{\cdot}09°$, and (2) *d*-menthone, $[\alpha]_D$ $+26{\cdot}85°$, gives the same compound, b. p. 121—124°/14 mm., D_4^{20} 0·9061, $[\alpha]_D$ $-2{\cdot}88°$. Saturation of these alcohols in the cold with hydrogen chloride gives the corresponding chlorides, which are transparent liquids and distil undecomposed under diminished pressure. Treatment of the chlorides with either silver carbonate or nickel carbonate yields 3-*allyl-Δ^3-menthene*,

$$CHMe{<}{\begin{matrix}CH_2{\cdot}C(CH_2{\cdot}CH{:}CH_2)\\CH_2\text{————————}CH_2\end{matrix}}{>}CPr^\beta.$$

b. p. 214—217°, or 97—100°/17 mm., the two preparations having the properties (1) D_4^{20} 0·8551, $[\alpha]_D$ $+50{\cdot}86°$, and (2) D_4^{20} 0·8552, $[\alpha]_D$ $+45{\cdot}06°$; oxidation of the hydrocarbon by permanganate in neutral solution gives a polyhydric alcohol, acetone and acetic, *iso*-butyric and β-methyladipic acids.

Oxidation of 3-allylmenthanol by means of potassium dichromate and sulphuric acid yields acetone and acetic, *iso*butyric, and β-methyladipic acids, and that of 3-methyl-3-allyl*cyclo*hexanol, acetic and methyladipic acids.

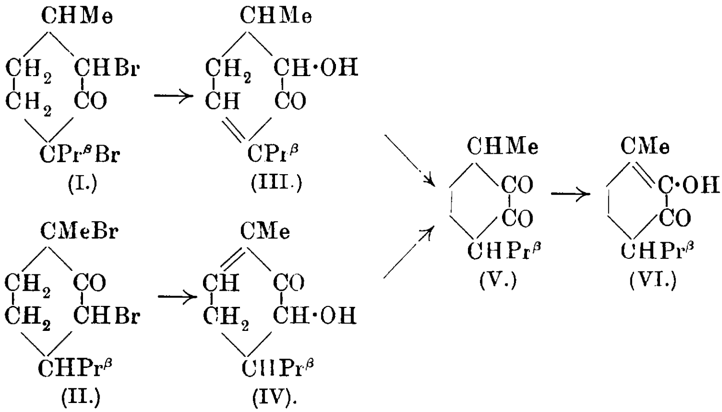
1-*Methyl-3-allyl-Δ^3-*cyclo*hexene*, obtained by converting the inactive 3-methyl-1-allyl*cyclo*hexanol into the corresponding chloride and treating the latter with silver carbonate, is a liquid, b. p. 171—173°, D_4^{20} 0·8361, $[\alpha]_D$ $+52{\cdot}84°$, and yields a polyhydric alcohol and β-methyladipic acid when oxidised by permanganate.

In the preparation of the above alcohols from ketones by means of zinc and allyl iodide, the resultant product was decomposed by water and distilled in a current of steam, the addition of sulphuric acid being avoided in order to preserve the stereochemical structure of the ketone from secondary influences.

The results obtained, which are to be described more in detail later, support Beckmann's view that *d*- and *l*-menthones are not mirror-images. T. H. P.

Reduction and Oxidation Processes in the Terpene Group. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 520—527). —It has been shown (A., 1914, i, 303, 556) that, on direct bromination, menthone and tetrahydrocarvone yield respectively compounds (I) and (II), and that each of these gives buchu-camphor

(VI) when treated with dilute alkali hydroxide solution. It is suggested that these changes take place according to the scheme:



The present work was carried out with the object of testing the accuracy of this interpretation, especially as regards the conversion of the unsaturated alcohols, (III) and (IV), into the saturated ketone (V). Attempts have been made to eliminate halogens from halogenated terpenic ketones by the action of alkali, and thus to obtain compounds containing a secondary carbinol group and a double linking in one and the same nucleus, as in (III) and (IV).

The first compound to be employed is the tribromotetrahydrocarvone obtained by Wallach (A., 1895, i, 621) from 1 : 8-dibromotetrahydrocarvone, and regarded as the 1 : 3 : 8-compound, and consequently a derivative of compound II. In contact with 2·5% aqueous alkali hydroxide solution, this compound reacts quantitatively in the cold thus: $C_{10}H_{15}OBr_3 + 4NaOH = C_{10}H_{17}O_4Na + 3NaBr + H_2O$. The product thus formed is the sodium salt of an aliphatic, monocarboxylic acid containing a double linking and two hydroxyl groups, and, when treated in dilute acetic acid solution with lead peroxide, yields carbon dioxide and ζ-methyl-Δ^{ϵ}-hepten-β-one, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$, the latter being given in quantitative yield when the sodium salt is heated at above 250°. In aqueous solution and in presence of platinum-black, this sodium salt absorbs two atoms of hydrogen, and the new salt thus formed furnishes ζ-methylheptan-β-one quantitatively when heated. The conclusion is drawn that the acid, $C_{10}H_{18}O_4$, is an αβ-dihydroxycitronellic acid, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe(OH){\cdot}CH(OH){\cdot}CO_2H$. The first step in the formation of this acid by the action of alkali on 1 : 3 : 8-tribromotetrahydrocarvone is represented thus:

$$CMeBr{<}{\begin{matrix}CO{\cdot}CHBr\\CH_2{-}{-}CH_2\end{matrix}}{>}CH{\cdot}CMe_2Br \longrightarrow$$

$$OH{\cdot}CMe{<}{\begin{matrix}CO{\cdot}CH(OH)\\CH_2{-}{-}{-}{-}CH_2\end{matrix}}{>}C{:}CMe_2.$$

The latter, then, either (1) undergoes hydrolysis between carbon atoms 3 and 4, giving the hydrated aldehyde,

$$CMe_2\!:\!CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CO\cdot CH(OH)_2,$$

which changes into the dihydroxycitronellic acid by reciprocal reduction and oxidation of the carbonylic and aldehydic groups, or (2) undergoes hydration and subsequent dehydration, giving the tautomeric compound, $OH\cdot CMe{<}{\begin{matrix}CH(OH)\cdot CO\\ CH_2\text{---}CH_2\end{matrix}}{>}C\!:\!CMe_2$, which then undergoes hydrolysis between carbon atoms 3 and 4. Scheme (2) is the more in accord with the mobility of terpene molecules.

In the preparation of tribromotetrahydrocarvone, the latter is accompanied by a liquid, which under the action of sodium hydroxide gives (1) the sodium salt, $C_{10}H_{17}O_4Na$, (2) a *compound*, $C_{10}H_{14}O_2$, which forms shining, white needles, m. p. 76°, has a phenolic odour, and gives a violet-black coloration with aqueous ferric chloride.

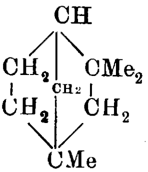
The *sodium*, *sodium hydrogen*, *barium* ($+2H_2O$), and *silver* salts of dihydroxycitronellic acid were prepared, and the *sodium* and *silver* salts of the acid, $C_{10}H_{20}O_4$, obtained on reduction. T. H. P.

Bromocamphorsulphonic Acid and Oxonium Compounds. D. McIntosh (*Trans. Roy. Soc. Canada*, 1915, [iii], **9**, (3), 85—86).—The author has unsuccessfully attempted to resolve the additive compounds of methyl ethyl ether with halogen hydracids into the corresponding dextro- and lævo-stereoisomerides, by the crystallisation of a supersaturated ethereal solution at low temperature. Bromocamphorsulphonic acid might be expected to produce more stable oxonium compounds with alcohols and ethers than do the halogen hydracids, but unfortunately no indication of the formation of oxonium compounds between this acid and alcohol or ether was observed.

In the opinion of the author the compounds formed by dimethylpyrone with halogen acids are not oxonium salts, but molecular compounds containing acid of crystallisation, and therefore do not contain asymmetric oxygen. D. F. T.

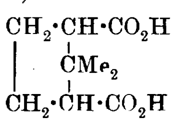
Fenchone Derivatives. S. S. Nametkin (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1590—1606).—Various authors have prepared saturated bicyclic hydrocarbons, $C_{10}H_{18}$, to which the name fenchane has been given, their properties being as follows: (1) b. p. 162·5—163·5°/751 mm., D_4^{20} 0·8550, n^{20} 1·4560, $[\alpha]_D$ −8°16′ (Zelinski, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 770); (2) b. p. 151·5°/763 mm., D_4^{20} 0·8325, n^{20} 1·4463, $[\alpha]_D$ −16·53° (Kishner and Proskurjakov, A., 1911, i, 680); (3) b. p. 149°/750 mm., D_4^{20} 0·8316, n^{20} 1·4462, $[\alpha]_D$ −18·1° (Wolff and Nolte, A., 1912, i, 988); (4) b. p. 162—163°/737·8 mm., D^{20} 0·8733, n^{17} 1·4541, $[\alpha]_D$ −19·83° (Ipatiev and Matov, A., 1913, i, 65). It is evident that the name fenchane has been given to at least two different hydrocarbons, and this name should be retained only where the bicyclic system of the compound is identical with that of fenchone. Such may be assumed to be the case with the hydrocarbons (2) and (3), which are obtained

from the ketone in conditions under which no rearrangement has yet been observed. In the case of compounds (1) and (4), however, their preparation is undoubtedly accompanied by isomerisation of the bicyclic system of fenchyl alcohol; that this is so follows from the analogous transformations of borneol, from which Zelinski and Čelikov (A., 1902, i, 2) obtained "liquid camphene" instead of bornylene, and Ipatiev and Matov (*loc. cit.*) *iso*camphane instead of camphane. Further proof of these relations is advanced in the present paper.

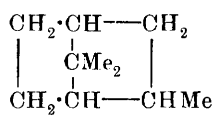


Assuming Semmler's formula for fenchone, the corresponding saturated, bicyclic hydrocarbon (annexed formula) should, from analogy with similar cases (A., 1915, i, 698, 699, 700, 701), give only a secondary nitro-compound when treated with dilute nitric acid in a sealed tube; no tertiary nitro-product should be formed, since the only tertiary hydrogen atom, being united to a carbon atom common to both rings, should not be replaced by a nitro-group under the conditions of Konovalov's reaction. This is actually found to be the case with the hydrocarbon prepared from fenchone by Kishner's method, the neutral products of the nitration containing only secondary nitro-compounds and a ketone. Just as was found with camphenilane (A., 1915, i, 699, 701), the action of nitric acid on fenchane is directed simultaneously and independently towards both rings, the products being nitro-compounds corresponding with the initial fenchone and with *iso*fenchone respectively. These two nitro-compounds have not been isolated in the pure state, but the ketones prepared from them, *d*-fenchone and *l*-*iso*fenchone, have been investigated. In this way is established the identity of the three bicyclic systems: Kishner and Proskurjakov's fenchane, natural fenchone, and Bertram and Helle's *iso*fenchone (A., 1900, i, 398). The acid layer from the nitration of fenchane yields crystalline *iso*fenchocamphoric acid; the formation of this acid, which is 1:3:3-trimethyl*cyclo*pentanedicarboxylic acid, from fenchane renders possible the simplification of its name to fenchocamphoric acid.

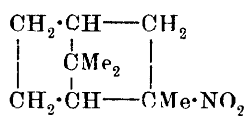
The examination of Zelinski's hydrocarbon is not yet complete, but the results now obtained indicate the presence of a bicyclic system quite different from that of fenchone. The principal product of the nitration with dilute nitric acid is in this case a typical tertiary nitro-compound, whilst the acid layer contains *apo*camphoric acid (annexed formula I). From this it is evident that Zelinski's dihydrofenchene is 2:7:7-trimethyl-[1:2:2]-*bicyclo*pentane, and may be called shortly "*iso*bornylane" (annexed formula II):



(I.)



(II.)

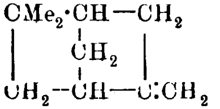


(III.)

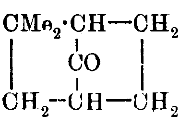
By analogy from the behaviour of *iso*camphane, secondary pro-

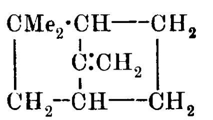
cesses, combined with the formation of a hemicyclic double linking, might be expected to accompany the formation of the tertiary nitro-compound (III). Since experiment does not confirm such expectation, this complication of Konovalov's reaction cannot be regarded as general for saturated bicyclic hydrocarbons.

By oxidising a mixture of fenchenes with permanganate, Wallach obtained two α-hydroxy-acids, m. p. 152—153° and 138—139°. Further oxidation of the latter yields a fenchocamphorone, m. p. 62—63°, and treatment of this with nitric acid (D 1·25) appears to give only dimethylsuccinic acid. For the corresponding fenchene, termed *iso*fenchene, Semmler (" Aetherische Öle," III, 550) suggests the annexed formula, from which it follows that this second camphorone should be identical with Hintikka and Komppa's α-*iso*camphenilone (A., 1912, i, 278), whereas actually these two ketones show marked differences in all their properties.



If, indeed, this fenchocamphorone has the structure of 5 : 5-dimethyl-[1 : 2 : 2]-*bicyclo*heptan-2-one, its oxidation should yield, not dimethylsuccinic acid, but *apo*fenchocamphoric acid (A., 1915, i, 701). It is evident, therefore, that Wallach's second fenchocamphorone and the corresponding hemicyclic fenchene cannot have the structures assigned to them by Semmler and his school (compare Bartelt, " Die Terpene und Campherarten," 1908, 95). Since, further, this fenchocamphorone is not identical with either of the two other known 5 : 5-dimethyl-[1 : 2 : 2]-*bicyclo*heptanones, namely, camphenilone and β-*iso*camphenilone (A., 1915, i, 701), the only possible structures for it and the corresponding fenchene are the annexed ones, the assumption being made that the 5 : 5-dimethyl-[1 : 2 : 2]-*bicyclo*heptanone grouping persists in them.





[With (MLLES.) V. S. MANUILOVA and T. I. MACÉEVSKAJA.]—The two nitro-derivatives, $C_{10}H_7 \cdot NO_2$, obtained by the action of nitric acid (D 1·075) on Kishner and Proskurjakov's hydrocarbon, have the properties: (1) b. p. 84—85°/1·3 mm., D_4^{20} 1·0396, n_D^{20} 1·4759, $[\alpha]_D$ +15·5° (in alcohol); this consists of a mixture of at least two isomerides: 2-nitrofenchane, corresponding with fenchone, and 6-nitrofenchane, corresponding with *iso*fenchone; (2) b. p. 139·5—140°/40 mm., D_4^{20} 1·0351, n_D^{20} 1·4742, $[\alpha]_D$ −12·48°; since oxidation with alkaline permanganate gives a ketone corresponding in properties with *iso*fenchone and yielding fenchocamphoric acid on further oxidation, this nitro-compound represents one of the stereoisomeric 6-nitrofenchanes.

The dibasic acid, $C_{10}H_{16}O_4$, also formed in this action consists of a mixture of *cis*- and *trans*-fenchocamphoric acids, the former predominating (compare Sandelin, A., 1913, i, 469); the *cis*-*l*-acid was separated by means of its anhydride. The ketonic products consist of a mixture of *d*-fenchone and *l*-*iso*fenchone.

[With (MLLE.) L. N. ABAKUMOVSKAJA].—*iso*Bornylane was obtained as follows: Fenchone was reduced by means of sodium in alcoholic solution to fenchyl alcohol, m. p. 45°, $[\alpha]_D$ −11·18° (in alcohol), which when heated at 265° with phthalic acid gave fenchene, $C_{10}H_{16}$, b. p. 152—157°/750 mm., D_4^{20} 0·8616, n_D^{20} 1·4642, $[\alpha]_D$ −4·51°. Hydrogenation of the fenchene at 165° by Sabatier and Senderens' method gave *iso*bornylane, $C_{10}H_{18}$, b. p. 163·5—164·5°/753 mm., D_4^{20} 0·8579, n_D^{20} 1·4590, $[\alpha]_D$ −12·36°, with a faint odour recalling that of *iso*camphane. When heated with nitric acid (D 1·075) at 130—135°, *iso*bornylane yields: (1) the tertiary *nitro*-compound (formula III, above), which is a colourless oil, b. p. 113—114°/12 mm., D_4^{20} 1·0575, n_D^{20} 1·4813, $[\alpha]_D$ −26·72° (in alcohol). On reduction it gives the corresponding *amine*, $C_{10}H_{17}\cdot NH_2$, which is a colourless liquid, b. p. 199—199·5°/756 mm., D_4^{20} 0·9171, n_D^{20} 1·4800, $[\alpha]_D$ −6·24° (in alcohol), with the characteristic odour of aliphatic amines, and absorbs carbon dioxide with avidity; its *benzoyl* derivative, $C_{10}H_{17}\cdot NHBz$, forms crystals, m. p. 134—135°. (2) *apo*Camphoric acid (*vide supra*). T. H. P.

β-Phellandrene. L. FRANCESCONI and E. SERNAGIOTTO (*Gazzetta*, 1916, **46**, i, 119—127).—The essential oil of *Bupleurum fruticosum* gives a nitrosochloride of almost constant specific rotation, but in a yield which increases with diminution of the specific rotation of the fraction of the oil employed. Since α-phellandrene does not form a nitrosochloride under the same experimental conditions as the β-isomeride, it seemed probable that the specific rotation of the latter has a value about equal to those given by Pesci (A., 1886, 1038), Wallach (A., 1904, i, 1035), and Schimmel, namely, +14·45° to +18·54°, and that a second terpene, probably α-phellandrene, is also present in considerable proportions in the more highly dextrorotatory fractions of the oil. It is found, however, that the yield of nitrosite and also its specific rotation are constant with the different fractions of the essential oil. The conclusion is therefore drawn that the specific rotation of β-phellandrene is at least 65·02°, which is the maximum observed value for the oil, and that the fractions exhibiting lower activity are mixtures of the two optical antipodes with the dextrorotatory form always preponderating. This view is supported by the fact that identical products, namely, tetrahydrocuminaldehyde and β-*iso*propyladipic acid, are obtained on oxidising two fractions of the oil, with specific rotations of +65° and +19° respectively, by means of permanganate under the conditions employed by Wallach (*loc. cit.*). T. H. P.

The Essential Oil of Eucalyptus Smithii from Various Forms of Growth. HENRY G. SMITH (*J. Roy. Soc. New South Wales*, 1915, **49**, 158—168, with 14 plates).—As the time seems to be approaching when a choice will have to be made of the best species of eucalypts for cultivation, attention is called to *E. Smithii*, the leaves of which produce one of the best cineol-pinene eucalyptus oils yet examined. The tree is valueless for timber, but is remarkably virile, and seems to flourish after repeated loppings. Indeed, it is best to cultivate the "suckers" which rapidlv grow out of the

stumps of the felled mature trees, as these produce more leaves and are more easily harvested.

The oil contains a very high percentage of cineole, also pinene, a phenol, *d*-eudesmol, m. p. 79°, a paraffin, m. p. 64°, a small quantity of esters and of a sesquiterpene, and a small amount of volatile aldehydes which soon disappear and change into agreeable sweet-briar-like perfumes. The oil is almost free from objectionable constituents, and may be purified without distillation, merely by shaking it with very dilute sulphuric acid for some hours and then with anhydrous sodium carbonate.

From an evaluation of oils obtained from various growths, it may be accepted that the cultivated trees can be profitably cut at three years old, and then every two years. J. C. W.

Gynocardia and Chaulmoogra Oils, and Gynocardic and Chaulmoogric Acids. M. A. RAKUZIN and G. D. FLIER (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1848—1851).—Ostromisslenski and Bergman (A., 1915, i, 646) refer to gynocardia oil and chaulmoogra oil as identical. These oils have, indeed, often been confused, and investigation of products sold as gynocardia oil and gynocardic acid showed that these were actually chaulmoogra oil and chaulmoogric acid respectively; the latter have the respective specific rotations, $+51\cdot8°$ and $+55\cdot5°$, whereas the *Gynocardia* products are optically inactive. The healing properties in cases of leprosy probably belong to chaulmoogric, and not to gynocardic acid.
T. H. P.

New Syntheses of Caoutchouc and its Homologues. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1910—1915).—Much of the work published since 1911 on the polymerisation of the diolefines is inaccurate, and many of the patents are useless. In the succeeding papers the author describes: (1) peculiar processes of isomerisation of two different forms of isoprene caoutchouc, and (2) methods for the catalytic polymerisation of diolefines to both normal and abnormal caoutchoucs; these methods give nearly or quite quantitative yields. T. H. P.

Synthesis of the *s*-Bromide of Erythrene Caoutchouc, of the Caoutchouc itself, and of Caouprene. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1915—1927).—Caouprene bromide is shown to be identical with the *s*-bromide of erythrene caoutchouc. Removal of hydrogen bromide from either caouprene bromide or the *as*-bromide of erythrene caoutchouc yields dehydrocaouprene, $C_{32}H_{48}Br_{16}-16HBr=C_{32}H_{32}$, and a homologous compound, $C_{32}H_{24}Me_8$, is similarly obtained from the bromide of natural Para caoutchouc, $C_{32}H_{40}Me_8Br_{16}$. Cryoscopic determination of the molecular weight of the readily soluble modification of caouprene bromide (α) in ethylene bromide gives the value 1809, in agreement with the above formula. When forced through a capillary dipping into alcohol or glacial acetic acid, the asymmetric bromide of erythrene caoutchouc or caouprene bromide in concentrated solution

is precipitated as a continuous white thread, but this exhibits little strength and no silky lustre. Caouprene bromide is regarded as having the structure, $\begin{array}{l} CHBr\cdot[CH_2\cdot CHBr]_7\cdot CH_2 \\ CH_2-[CHBr-CH_2]_7-CHBr \end{array}$.

Reduction of caouprene bromide by means of zinc dust yields erythrene caoutchouc and, in greater or less proportion, the isomeric caouprene, $C_{32}H_{48}$, which has one of the constitutions:

$$\begin{array}{l} CH_2{:}C-CH_2-CH\cdot CH_2\cdot CH\cdot \;\ldots\; \cdot CH\cdot CH_2\cdot CH_2 \\ \quad\;\; CH_2\cdot CH_2\cdot CH\cdot CH_2\cdot CH\cdot \;\ldots\; \cdot CH\cdot CH_2\cdot C{:}CH_2 \end{array},$$

$$CH_2{<}\begin{array}{l} CH\cdot CH_2\cdot CH\cdot CH_2\cdot CH\cdot \;\ldots\; \cdot CH\cdot CH_2\cdot CH \\ CH\cdot CH_2\cdot CH\cdot CH_2\cdot CH\cdot \;\ldots\; \cdot CH\cdot CH_2\cdot CH \end{array}{>}CH_2,$$

or

$$\begin{array}{l} CMe\cdot CH_2\cdot CH\cdot CH_2\cdot CH\cdot \;\ldots\; \cdot CH\cdot CH_2\cdot CH \\ CH-CH_2-CH\cdot CH_2\cdot CH\cdot \;\ldots\; \cdot CH\cdot CH_2\cdot CMe \end{array}.$$

Caouprene is transparent, and forms either a viscous liquid or an amorphous, elastic mass; on dry distillation it yields carbon and hydrogen almost quantitatively, and when heated at 60—70° with benzoyl peroxide is converted into normal erythrene caoutchouc. It was ozonised in chloroform solution, but decomposition of the ozonide by water gave no definite product; its tetrabromide and dihydrochloride were prepared.

The action of zinc dust on the asymmetric bromide of natural or synthetic caoutchouc in presence of alcohol gives the free caoutchouc, $C_{32}H_{48}Br_{16} + 8Zn = 8ZnBr_2 + C_{32}H_{48}$. This reaction has been used for the recovery of rubber from the bromide of Para caoutchouc. T. H. P.

Synthesis of Natural Caoutchouc by Way of β-Myrcene. I. I. OSTROMISSLENSKI and F. F. KOSCHELEV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1928—1931).—When cautiously heated at 80—90°, isoprene yields an open-chain, myrcene-like hydrocarbon, $C_{10}H_{16}$, which contains three double linkings, two of them in conjugated positions, and is termed *β-myrcene*. The latter is a colourless, mobile liquid, b. p. 63—63·5°/20 mm., 58°/13 mm., D_4^{20} 0·8472, n_D^{26} 1·53681. When heated at 60—70° with barium peroxide and sodium, β-myrcene is converted quantitatively into normal isoprene caoutchouc, whereas under similar conditions isoprene gives an abnormal caoutchouc. The most probable constitution of β-myrcene is $CH_2{:}CH\cdot CMe{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CH_2$. Unsuccessful attempts were made to avoid the use of isoprene and to prepare the hydrocarbon by dehydration of the corresponding alcohols of the terpene series. T. H. P.

Structure of Caoutchoucs. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1932—1936).—The bromide of natural caoutchouc, being homólogous with caouprene bromide, has a unicyclic structure, $[\cdot CH_2\cdot CH_2\cdot CMeBr\cdot CHBr\cdot]_x$, and since, under the action of zinc dust, it is converted readily and quantitatively into

the free caoutchouc, the latter will also possess a unicyclic structure, namely, $[\cdot CH_2\cdot CH_2\cdot CMe\colon CH\cdot]_x$ (compare Pickles, T., 1910, **97**, 1085); the positions of the methyl groups and double linkings in this formula are established by the products of decomposition, namely, lævulinaldehyde and lævulic acid. In the case of normal isoprene caoutchouc, prepared by direct heating of isoprene, the grouping of the methyl radicles and ethylenic linkings must be different from that given above, since decomposition of the corresponding ozonide by means of water yields, not only lævulinaldehyde and lævulic acid, but also succinic acid and acetonylacetone. Willstätter has shown that multiple-membered, unicyclic groupings of unsaturated hydrocarbons are readily transformed into polycyclic groupings, and Harries has proposed for natural caoutchouc a structure in which such isomerisation is assumed. That both free caoutchouc and also its halogenides and hydrohalogenides possess, however, unicyclic structures, and are not polymerides of the corresponding *cyclo*octadiene, is, however, shown by the following facts: (1) Caoutchouc bromide and hydrobromide have the respective compositions $C_{32}H_{40}Me_8Br_{16}$ and $C_{32}H_{40}Me_8(HBr)_8$, and not $C_{32}H_{40}Me_8Br_4$ and $C_{32}H_{40}Me_8(HBr)_2$. The action of halogens on caoutchouc is not accompanied by depolymerisation of the molecule, since erythrene caoutchouc bromide has the molecular weight 1809, corresponding with the formula $C_{32}H_{48}Br_{16}$, and readily regenerates the free caoutchouc when treated with zinc dust. (2) Dimethyl*cyclo*octadiene tetrabromide, described by Willstätter, is a crystalline compound with a sharp melting point, and has no properties comparable with those of caoutchouc bromide. (3) Polymerisation of *cyclo*octadiene occurs with almost explosive readiness, and yields crystalline and horny compounds, but no trace of caoutchouc. On the other hand, in no case does the depolymerisation of caoutchoucs or any of their other reactions give rise to *cyclo*octadiene derivatives. T. H. P.

Polymerisation of Ethylenic Compounds and Mechanism of the Conversion of Vinyl Bromide into the Bromide of Erythrene Caoutchouc. I. I. Ostromisslenski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1937—1941).—The conversion of unsaturated compounds into ring compounds is completely analogous to the process of polymerisation, the molecule first undergoing decomposition into a hydrogen atom and a free radicle, the affinities of which are immediately satisfied by the double linking of the same molecule. Thus, the cyclisation of unsaturated compounds may be regarded as a process of intramolecular polymerisation. At the moment when the trimeride appears, the polymerisation of vinyl bromide proceeds in two directions: (1) A small part of the trimeride undergoes intramolecular polymerisation, with formation of the stable, six-membered ring compound, 1:3:5-*tribromo*cyclo*hexane*,

$$CHBr<\begin{matrix}CH_2\cdot CHBr\\ CH_2\cdot CHBr\end{matrix}>CH_2,$$

which is an oily liquid, b. p. 154—158°/13 mm., and is converted into benzene when heated with quinoline. (2) The remainder of the trimeride unites with unchanged monomeride until a 32-mem-

bered chain of carbon atoms is formed, this then undergoing cyclisation to form the symmetrical bromide of erythrene caoutchouc. T. H. P.

Mechanism of the Conversion of Isoprene into Caoutchouc and Conversion of β-Myrcene into Caoutchouc. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1941—1947).—The discovery by the author and Koschelev (this vol., i, 274) of the formation of β-myrcene in the process of conversion of isoprene into caoutchouc throws light on the mechanism of this process. In the first place, the hydrogen atom and the residual radicle from a molecule of isoprene combine at the ethylene linking of a second molecule, giving the dimeride, β-myrcene. The latter is then converted into the trimeride, and so on until the octameride is formed, this then undergoing "intramolecular polymerisation" or cyclisation to isoprene caoutchouc. As was shown by Steimmig (A., 1914, i, 307), all the polymerides of isoprene yet obtained differ from natural Para caoutchouc, since the decomposition of their ozonides by water yields acetonylacetone and succinic acid, in addition to lævulinaldehyde and lævulic acid. Theoretically, β-myrcene may, like isoprene, dissociate into a hydrogen atom and a radicle in different ways, and experiment shows that, under the action of barium peroxide and sodium, pure β-myrcene is converted quantitatively into normal isoprene caoutchouc, which has an elasticity point considerably below 0° and coincident with that of natural caoutchouc; on the other hand, a mixture of 90% of isoprene with 10% of β-myrcene gives, under the same conditions, a quantitative yield of an isomeric, abnormal caoutchouc, the elasticity point of which is +110°. This polymerisation of chemically pure β-myrcene may possibly represent the only synthesis of natural caoutchouc, that is, of a substance perfectly identical with Para caoutchouc, both in the general structure of its nucleus and also in the positions of the methyl groups and double linkings of the molecule.

There is reason to believe that tropical plants synthesise caoutchouc by means of β-myrcene or myrcene-like hydrocarbons or their dimerides, and not by the polymerisation of isoprene. Thus, the sap of plants frequently contains compounds with an atom-grouping like that of myrcene, such as geraniol, linalool, nerol, etc., and simple dehydration of these unsaturated alcohols would lead immediately to the corresponding myrcenes.

A very close analogy exists between the polymerisation of isoprene and that of vinyl bromide. Each gives cyclic compounds of two types, one 6-membered and the other 32-membered; the former are dipentene and tribromo*cyclo*hexane respectively, and the latter, caoutchouc and the bromide of erythrene caoutchouc. T. H. P.

Cold Vulcanisation of Caoutchouc by Means of Sulphur, or Trinitrobenzene, or Benzoyl Peroxide. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1885—1892).—It has been previously shown (*ibid.*, 1915, **47**, 1441) that a mixture of a primary or secondary aliphatic amine with a metallic oxide either accelerates

the vulcanisation of natural and synthetic caoutchoucs or considerably lowers the temperature of vulcanisation. It is now found that, in presence of such mixtures, vulcanisation takes place at the ordinary temperature, this process being especially rapid with chemically pure caoutchoucs, such as normal erythrene or normal isoprene caoutchouc, obtained synthetically; with natural caoutchoucs the vulcanisation requires two to six months. In either case the change is greatly accelerated by preliminary heating of the mixture at 40—60° for ten to forty minutes, vulcanisation then being completed in ten to forty-eight hours. Since the volume changes either not at all or but negligibly at the ordinary temperature, the use of special metallic moulds is rendered unnecessary. Vulcanisation by means of 1 : 3 : 5-trinitrobenzene or benzoyl peroxide also takes place at the ordinary temperature, no special catalyst being required. Oxides of zinc, magnesium, and, particularly, lead accelerate the action when the nitro-compound is used, but these oxides retard cold vulcanisation by benzoyl peroxide and diminish the value of the vulcanised product. T. H. P.

Mechanism of the Action of Amines and Metallic Oxides on the Vulcanisation of Caoutchouc. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1892—1898).—With a mixture of caoutchouc, sulphur, amine, and metallic oxide, the sulphur and the amine first react with formation of the corresponding thiozonide, $R{\cdot}NH_2 + 4S = NHR{\cdot}S{\cdot}S{\cdot}S{\cdot}NHR + H_2S$, this reaction proceeding only in presence of a catalyst such as an oxide. The unstable thiozonide then transmits its sulphur to the caoutchouc, the amine being regenerated, or the aminic residue, under the influence of the oxide, uniting with a fresh portion of sulphur to give thiozonide. Thus, the process is one of double catalysis: the metallic oxide catalyses the formation of the thiozonide of the amine, which, in its turn, accelerates the formation of the caoutchouc thiozonide, and so catalyses the vulcanisation. Only primary and secondary amines give thiozonides, and these are the only amines which catalyse the vulcanisation of caoutchouc. Thiozonides of aromatic amines, which are formed according to the equations (1) $2NH_2Ph + 4S = NHPh{\cdot}S{\cdot}S{\cdot}S{\cdot}NHPh + H_2S$, and

(2) $NHPh{\cdot}S{\cdot}S{\cdot}S{\cdot}NHPh = NH_2{\cdot}C_6H_4{\cdot}S{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}NH_2$,

are relatively stable compounds and should therefore be incapable of functioning as sulphur-carriers; an explanation is thus afforded of the observation that aromatic amines have practically no catalysing action on the vulcanisation of caoutchouc.

From Bernstein's observation that the ordinary vulcanisation of caoutchouc proceeds at the ordinary temperature under the action of ultraviolet light (A., 1913, i, 638, 746), the conclusion is drawn that, in absence of air, this light activates sulphur by converting it into thiozone, S_3; the vulcanisation is then effected partly by the latter and partly by the ozone formed simultaneously. It is shown experimentally that thiozone is also formed when ordinary sulphur is dissolved in a primary or secondary aliphatic amine, such as piperidine with a side-chain, and the solution either heated for twenty to

fifty minutes with lead oxide in a reflux apparatus on a water-bath or left at the room temperature. If, as Erdmann supposes (A., 1908, ii, 830), sulphur dyes are either stable thiozonides or products of their decomposition, condensation, etc., the presence of a mixture of amine and oxide should lower the temperature of formation of these dyes almost to the ordinary temperature or should accelerate their formation at higher temperatures. Such a mixture should cheapen and simplify the production of some of these dyes, and should lead to the isolation of a new series of ozonides unobtainable at the higher temperatures and with prolonged heating. T. H. P.

Vulcanisation of Caoutchouc by Means of Halogenated Compounds. Mechanism of Vulcanisation. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1898—1904).—In the formation of vulcanite-like substances by the action of bromine, iodine, or iodine bromide on caoutchouc, the first phase of the change undoubtedly consists in the formation of the caoutchouc halogenide, the unchanged caoutchouc then either adsorbing this new compound or swelling into it. It is, indeed, found that this process may also be carried out by treatment of the caoutchouc with its halogenide, the latter acting when either freshly prepared or old. All three halogenides of either natural or synthetic caoutchouc may be employed. It is found, further, that caouprene chloride or bromide exerts a similar action in caoutchouc, the products obtained from the chloride being especially valuable in view of their great stability and relatively low elastic point and of the fact that they are usually obtained in chemically pure condition. The amount of caoutchouc used need not exceed 7—10 parts per 100 parts of caouprene chloride, the cost of the ebonite obtained being thus considerably reduced. Similar vulcanisation is effected by the action of the hydrochloride of natural caoutchouc, but not by that of aluminium chloride. The products obtained by the above method have the black colour of ordinary ebonite, are electrical non-conductors, may be scratched with the nail, keep well even in moist air, and take a high polish. T. H. P.

Vulcanisation of Caoutchouc by Molecular Oxygen, Ozone, or Ozonides of Organic Compounds. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1904—1909).—The action of ozone in vulcanising caoutchouc rests on the preliminary formation of the ozonide of the caoutchouc. The ready-formed ozonide has, indeed, an effect similar to that of ozone, both soft and horny resins being formed; the course of the process is determined most of all by the concentration of the vulcanising compound. When caoutchouc is exposed in an atmosphere of dry air to the ultraviolet rays of a quartz mercury lamp, it undergoes gradual vulcanisation, increasing in weight at the expense of the oxygen; at 40—80° this process takes place fairly rapidly, but at 120° no vulcanisation occurs. Vulcanisation of caoutchouc by means of its ozonide takes place under the same conditions as vulcanisation by benzoyl peroxide.

In presence of moisture, chemically pure caoutchouc activates molecular oxygen, and thus behaves like most of the terpenes. Thus, moist isoprene (or erythrene) caoutchouc of the normal series, when left in the air at the ordinary temperature, gradually becomes covered with a layer of new, less elastic substance, this process being analogous to the drying of vegetable oils. If normal erythrene caoutchouc, coated in this way, is passed between cold rolls to render it as homogeneous as possible and then heated in the ordinary way in absence of air, the unchanged caoutchouc undergoes vulcanisation; if, however, this surface is first removed, vulcanisation does not take place. It is evident that this layer, consisting of a product of the action of atmospheric oxygen on the caoutchouc, constitutes the vulcanising substance.

The vulcanisation of caoutchouc by its halogenides or ozonides is a purely physical process, and is comparable with the formation of celluloid; the latter process may, indeed, be regarded as vulcanisation of cellulose esters by camphor, etc. The large number of known vulcanising agents indicates that the chemical nature of these plays no determining part. All these agents form colloids with the caoutchouc, and it is by these colloids that vulcanisation is effected. T. H. P.

Preparation of Vulcanised Caoutchouc Coloured with Organic Pigments. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1993—1995).—Since organic pigments readily decompose at a high temperature, especially in presence of sulphur, the author's method of vulcanising at the ordinary temperature in presence of sulphur, an amine, and an oxide (this vol., i, 277) is of especial value in the manufacture of caoutchouc articles coloured with such pigments. Some of the latter are not decomposed when heated either at a comparatively low temperature or even at the temperature of ordinary vulcanisation, provided that this is maintained for only a short time; in such cases the author's process permits of the acceleration of the vulcanisation or of the lowering of the temperature employed. Experiments were made with eosin, erythrosin, alkali-blue, and cinnamylidenefluorene. T. H. P.

The Theory of the Acid Dye-bath. M. FORT (*J. Soc. Dyers*, 1916, **32**, 33—39).—It has been frequently assumed that the dyeing of wool by acid dyes is dependent on the liberation of the colour acid by the action of sulphuric acid on the sodium or other salt of the colour acid. Evidence is adduced in support of the view that this displacement of the colour acid from its salts plays no essential part in the process of dyeing by means of such acid dyes.

In the author's opinion the action of acids on wool results in the formation of salt-like compounds in which hydrolytic amino-products play the part of the base. These salts, which in the ordinary practice of the acid dye-bath consist of sulphates, react with the colour acid or its sodium salts in accordance with the equation wool base, H_2SO_4 + colour acid $\rightleftarrows$ wool base, colour acid + H_2SO_4; or wool base, H_2SO_4 + colour acid, Na $\rightleftarrows$ wool base, colour

acid + Na_2SO_4, the reactions in both cases being reversible. Quantitative experiments are described which are said to furnish evidence in support of this theory of acid dyeing.

The fact that it is much more difficult to dye cotton with acid dyes is well known, but by mordanting cotton with benzidine so as to give it a sufficiently pronounced basic character, it has been found possible to fix acid dyes on cotton with comparative ease. The attachment of the benzidine to the fibre is purely mechanical, but by the use of tannin-mordanted cotton, which readily takes up benzidine from a strong hot solution of the hydrochloride, very much better results have been obtained. H. M. D.

Colouring Matter of Cotton Flowers. III. ARTHUR GEORGE PERKIN (T., 1916, **109**, 145—154. Compare T., 1909, **95**, 2181; 1913, **103**, 650).—The author has examined the Egyptian and ordinary Indian yellow cotton flowers, *Gossypium herbaceum*, in order to ascertain whether they are chemically different, and whether the red, pink, and colourless petals of other varieties have any outstanding chemical characteristics.

It is found that the red flowers, *G. arboreum, Linn.*, contain *iso*quercitrin, but no other flavone glucoside, differing therefore from the yellow flowers, which also contain quercimeritrin and gossypitrin. The point has also been investigated whether the particular red pigment is an oxidation product of gossypetin or its glucoside, but the evidence obtained is inconclusive.

The yellow flowers, *G. neglectum*, from India, and also the ordinary yellow Indian flowers, *G. herbaceum*, are found to contain gossypitrin and *iso*quercitrin, but practically no quercimeritrin, which is an important constituent of the Egyptian flowers. Gossypitrin exists in two forms; if boiled with acetone or alcohol it has m. p. 200—202°, but after boiling with water it has m. p. 239—242°. The *acetyl* derivative, $C_{21}H_{11}O_{13}Ac_9$, forms colourless needles, m. p. 226—228°.

The white flowers, *G. neglectum* or *rossrum*, and the pink, *G. sanguineum*, are practically devoid of tinctorial properties.

Gossypitrin has been oxidised by alcoholic *p*-benzoquinone to the quinone, *gossypitrone*, $C_{21}H_{18}O_{13}$, which forms maroon-coloured needles, m. p. about 255—259°, and dyes aluminium mordanted calico green shades, and mordanted wool the same shades as gossypitrin. J. C. W.

Mechanism of the Formation of the Colouring Matter of Bile from the Ferruginous Components of the Colouring Matter of Blood. WILLIAM KÜSTER (*Arch. Pharm.*, 1916, **253**, 457—497) —A historical survey of the chemistry of hæmin and of bilirubin.

Although it is almost a matter of certainty that bilirubin, the colouring matter of bile, is produced from the hæmatin of the blood, the mechanism whereby the liver cells effect the change is still a mystery, and can only be thoroughly understood when the constitutions of the two substances are known. With the informa-

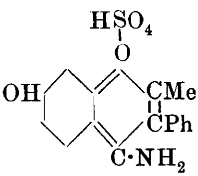
tion at present available, however, it is possible to trace paths along which the change may proceed. The author, therefore, discusses in some detail the investigations instituted since 1847 to throw light on the constitution of hæmin. The importance of hæmatic acid, hæmo-, crypto-, and phyllo-pyrroles and their carboxylic acids, and other fragments of the hæmin molecule is emphasised, and the way is indicated whereby from the known constitutions of these substances a formula for hæmin, such as that of Piloty, can be built up. Bilirubin and its fragments are treated in the same way, and formulæ for the colourless (?), orange, and reddish-brown modifications of bilirubin are built up. A comparison of these formulæ with that of hæmin indicates that bilirubin may be produced from hæmin by a fairly simple process of oxidation.

A full list of references to the literature is given at the end of the paper. C. S.

Valency of the Elements. IV. G. Povarnin (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2073—2115).—The author criticises Fahrion's oxidation theory of tanning (*Zeitsch. angew. Chem.*, 1909, **22**, 2083, 2135, 2187), and advances a theory based on the presence in all organic tanning materials of an active carbonyl group. T. H. P.

A Synthesis of Flavones. Brojendra Nath Ghosh (T., 1916, **109**, 105—122. Compare A., 1915, i, 831, 832).—Instead of using the esters of acetoacetic acids in the condensations with phenols, the nitriles have been employed. These react best with phenols containing methyl or hydroxyl substituents, giving imines, which can be hydrolysed to the flavones.

Condensations with Acetylphenylacetonitrile.—When mixed with resorcinol and concentrated sulphuric acid, the nitrile gradually deposited *4-imino-7-hydroxy-3-phenyl-2-methyl-γ-benzopyran*[*4-amino-7-hydroxy-3-phenyl-2-methyl-γ-benzopyrylium*] *sulphate* (annexed formula), in short, yellow needles, m. p. 246°. The free *base*, $C_{16}H_{13}O_2N,\frac{1}{2}H_2O$, formed brown prisms, m. p. 221° (decomp.), and yielded a *picrate*, orange-yellow needles, m. p. 227°, a *perchlorate*, yellow needles, an *acetyl* derivative, $\frac{1}{2}H_2O$, very pale yellow needles, m. p. 135°, and a *benzoyl* derivative, $\frac{1}{2}H_2O$, colourless needles, m. p. 178—179°. The constitution of the imine was proved by boiling the sulphate with 10% sulphuric acid, when 7-hydroxy-3-phenyl-2-methyl-γ-benzopyrone (*loc. cit.*) was produced.



The nitrile was also condensed with pyrogallol, with the formation of *4-imino-7:8-dihydroxy-3-phenyl-2-methyl-γ-benzopyran*,

$C_6H_2(OH)_2<\begin{matrix}O\text{———}CMe \\ C(:NH)\cdot CPh\end{matrix}$, in dark brown prisms, with $\frac{1}{2}H_2O$, m. p. 142° (decomp.). This yielded an *acetyl* derivative, pale yellow needles, m. p. 194°, and was hydrolysed to 7:8-dihydroxy-3-phenyl-2-methyl-γ-benzopyrone.

Condensation with α-naphthol gave rise to 4-*amino*-3-*phenyl*-2-*methyl*-1 : 4-α-*naphthapyrylium sulphate*, $C_{20}H_{15}ON,H_2SO_4$, which crystallised in bright orange needles, m. p. 174° (decomp.). The free *base* formed pale brown prisms, with $\frac{1}{2}H_2O$, m. p. 162°, and 3-phenyl-2-methyl-1 : 4-α-naphthapyrone was obtained on hydrolysis.

m-Cresol gave a small yield of 4-*amino*-3-*phenyl*-2 : 7-*dimethyl*-γ-*benzopyrylium sulphate*, $C_{17}H_{15}ON,H_2SO_4$, yellow prisms, m. p. 122°, which was converted into the free *base*, short, colourless needles, m. p. 89°, and into 3-*phenyl*-2 : 7-*dimethyl*-2-*benzopyrone*, $C_6H_3Me<\begin{matrix}O—CMe\\ CO\cdot CPh\end{matrix}$, colourless needles, m. p. 155°.

Condensations with Formylphenylacetonitrile.—Formylphenylacetonitrile was prepared by the addition of ethyl formate to a well-cooled solution of phenylacetonitrile and sodium in alcohol. It condensed with resorcinol under the influence of phosphoryl chloride with the formation of 4-*amino*-7-*hydroxy*-3-*phenyl*-γ-*benzopyrylium chloride*, $OH\cdot C_6H_3<\begin{matrix}OCl——CH\\ C(NH)_2\cdot CPh\end{matrix}$, which crystallised, with $1H_2O$, in short, dull yellow needles, m. p. 215° (decomp.). The free *base*, $C_{15}H_{11}O_2N,H_2O$, formed bright yellow needles, m. p. 226°, and yielded an *acetate*, $C_{17}H_{13}O_3N$, colourless needles, m. p. 186° (decomp.), a *benzoate*, $C_{22}H_{15}O_3N,H_2O$, m. p. 136°, and a *perchlorate*, bright yellow needles. The hydrochloride was also converted into 7-hydroxy-3-phenyl-γ-benzopyrone by hydrolysis.

Under similar conditions, the nitrile condensed with pyrogallol to form 4-*imino*-7 : 8-*dihydroxy*-3-*phenyl*-γ-*benzopyran*,

$$C_{15}H_{11}O_3N,H_2O,$$

yellow needles, m. p. 220°, which gave an *acetyl* derivative, colourless needles, with $1H_2O$, m. p. 171°, and, on hydrolysis, yielded 7 : 8-*dihydroxy*-3-*phenyl*-γ-*benzopyrone*, $C_{15}H_{10}O_4,2H_2O$, pale yellow needles, m. p. 215° (*acetyl* derivative, with $1H_2O$, m. p. 184°).

In the same way, orcinol gave rise to 4-*imino*-7-*hydroxy*-3-*phenyl*-5-*methyl*-γ-*benzopyran*, $C_{16}H_{12}O_2N,H_2O$, bright yellow needles, m. p. 235°, decomp. 241°, which was hydrolysed to 7-*hydroxy*-3-*phenyl*-5-*methyl*-γ-*benzopyrone*, $OH\cdot C_6H_2Me<\begin{matrix}O—CH\\ CO\cdot CPh\end{matrix}$, pale yellow needles, with $2H_2O$, m. p. 224°.

α-Naphthol was condensed with the nitrile under the influence of hydrogen chloride, giving 4-*amino*-3-*phenyl*-1 : 4-α-*naphthapyrylium chloride*, $C_{19}H_{13}ON,HCl,H_2O$, yellow needles, m. p. 135° (decomp.), from which the free *base*, dull yellow prisms, with $1H_2O$, decomp. 115—130°, and 3-*phenyl*-1 : 4-α-*naphthapyrone*,

$$C_{19}H_{12}O_2,\tfrac{1}{2}H_2O,$$

pale yellow needles, m. p. 169—170°, were prepared.

Condensations with Benzoylphenylacetonitrile.—The nitrile was prepared by adding ethyl benzoate to a solution of phenylacetonitrile and sodium in alcohol. It condensed with resorcinol under the influence of hydrogen chloride to form 4-*amino*-7-*hydroxy*-2 : 3-*diphenyl*-γ-*benzopyrylium chloride*, $C_{21}H_{15}O_2N,HCl,H_2O$, which

separated in pink needles, m. p. 286°. The free *base* crystallised in yellow needles, m. p. 290°, the *acetyl* derivative, $C_{23}H_{17}O_3N,\frac{1}{2}H_2O$, formed colourless needles, m. p. 215°, and the product of hydrolysis, namely, *7-hydroxy-2 : 3-diphenyl-γ-benzopyrone*, $OH\cdot C_6H_3<\begin{matrix}O-CPh\\ \|\\ CO\cdot CPh\end{matrix}$, separated in colourless needles, m. p. 288° (*acetyl* derivative, colourless leaflets, with $1H_2O$, m. p. 222°). The constitution of the pyrone was proved by decomposition with concentrated potassium hydroxide, when deoxybenzoin, resorcinol, and β-resorcylic acid were isolated from the products. An attempt was made to bring about the original condensation with the aid of concentrated sulphuric acid, but the nitrile was merely hydrolysed to the amide.

Pyrogallol condensed with benzoylphenylacetonitrile to form *4-imino-7 : 8-dihydroxy-2 : 3-diphenyl-γ-benzopyran*, $C_{21}H_{15}O_3N,\frac{1}{2}H_2O$, yellow needles, m. p. 179—180°, which was hydrolysed to *7 : 8-dihydroxy-2 : 3-diphenyl-γ-benzopyrone*, $C_{21}H_{14}O_6$, colourless needles, m. p. 185°.

Condensations with Benzoylacetonitrile.—This nitrile condensed with resorcinol in the presence of concentrated sulphuric acid to form *4-imino-7-hydroxy-2-phenyl-γ-benzopyran*, $C_{15}H_{11}O_2N,\frac{1}{2}H_2O$, yellowish-brown prisms, decomp. 185—235°, which yielded a *picrate*, orange needles, m. p. 238°, and gave 7-hydroxy-2-phenyl-γ-benzopyrone (Emilewicz and Kostanecki, A., 1898, i, 369) on hydrolysis with 5% sodium hydroxide, and acetophenone, resorcinol, and β-resorcylic acid when boiled with concentrated potassium hydroxide.

Similarly, α-naphthol yielded *4-amino-2-phenyl-1 : 4-α-naphthapyrylium sulphate*, $C_{19}H_{13}ON,H_2SO_4$, prisms, decomp. 185—215°; free *base*, pale brown prisms, decomp. 138—148°; *picrate*, orange needles, m. p. 274° (decomp.). On boiling with 5% sodium hydroxide, the amine gave a small yield of 2-phenyl-1 : 4-α-naphthapyrone (Kostanecki, A., 1898, i, 374).

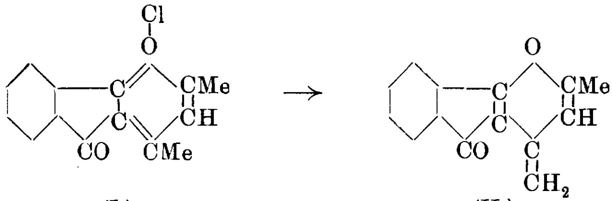
Pyrogallol gave rise to *4-imino-7 : 8-dihydroxy-2-phenyl-γ-benzopyran*, $C_{15}H_{11}O_3N,H_2O$, brown prisms, decomp. 145—165°.

J. C. W.

Synthesis of Ketoindopyranols. SOSALE GARALAPURY SASTRY and BROJENDRA NATH GHOSH (T., 1916, **109**, 175—180).—It has been shown that diketohydrindene suffers condensation with *o*-hydroxyaldehydes in the presence of an alkali (A., 1915, i, 1067). It does not react with diketones, like acetylacetone in an alkaline medium, but condensation takes place in the presence of hydrogen chloride. The ketones probably react in their enolic forms, for diketohydrindene also condenses under the same conditions with ketonitriles, behaving, therefore, like a phenol (compare preceding abstract).

Diketohydrindene condensed with acetylacetone in methyl-alcoholic hydrogen chloride to form *4′-keto-6-methyl-4-methylene-2 : 3-indenopyran(1 : 4) hydrochloride* [*5-keto-2 : 4-dimethyl-βγ-indenopyr-*

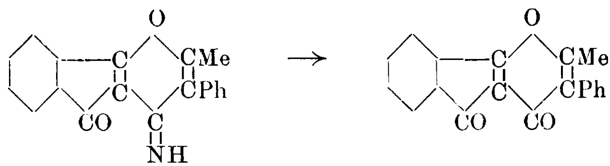
ylium chloride] (I), brown needles, m. p. 120°, from which the free *base* (II) was obtained, in brown prisms, m. p. 182°, by the action of sodium acetate. Similarly, benzoylacetone yielded 5-*keto*-



(I.) (II.)

2-*phenyl*-4-*methylene*-*βγ*-*indenopyran*, brown prisms, m. p. 219° (decomp.), and its *hydrochloride*, brown prisms, m. p. 190—200°.

Acetylphenylacetonitrile gave rise to 4-*imino*-4′-*keto*-5-*phenyl*-6-*methyl*-2:3-*indenopyran*(1:4) *hydrochloride* [4-*amino*-5-*keto*-3-*phenyl*-2-*methyl*-*βγ*-*indenopyrylium chloride*], dark red needles, m. p. 210° (decomp.), from which the *base* (III) was isolated in brown prisms, m. p. 222° (decomp.). The product was hydrolysed by boiling 10% sulphuric acid to 4:5′-*diketo*-3-*phenyl*-2-*methyl*-*βγ*-*indenopyran*(1:4) (IV), pale yellow needles, m. p. 256°:



(III.) (IV.)

J. C. W.

The Alkaloids of the Calabar Bean. V. Action of Phenylcarbimide: Phenyl Homologues of Eserine and Geneserine. MAX POLONOVSKI (*Bull. Soc. chim.*, 1916, [iv], **19**, 46—59. Compare A., 1915, i, 891, 892, 987; this vol., i, 221).—Phenylcarbimide condenses with eseroline and geneseroline in much the same way as does methylcarbimide, and the methods employed have been the same as those previously used in the latter case (*loc. cit.*).

When to eseroline (1 mol.) in ethereal solution, in the presence of a trace of sodium, phenylcarbimide (1 mol.) is added in benzene solution, and the solvent allowed to evaporate slowly, a crystalline compound, which the author calls *pheneserine*, is obtained in colourless prisms, m. p. 150°; $[\alpha]_D$ −80° in absolute alcohol. Its solutions are alkaline, but it does not give crystalline salts, except in the case of its *methiodide*, needles, m. p. 198°; $[\alpha]_D$ −92·8°. Pheneserine is insoluble in cold dilute alkalis, but is decomposed by hot alkalis, giving eseroline, aniline, and carbon dioxide. Analysis and estimation of the carbon dioxide thus liberated show that it has the composition $C_{13}H_{17}N_2$·O·CO·NHPh. If eseroline is heated with an excess of phenylcarbimide in benzene solution in a sealed tube at 100° for four hours, it yield *dipheneserine*, small needles, m. p. 184°;

$[\alpha]_D$ −244°. Its solutions are neutral, and it is soluble in warm concentrated acids, being reprecipitated by the addition of water. Its constitution is represented by

$$NHPh\cdot CO\cdot N\cdot C_{13}H_{16}N\cdot O\cdot CO\cdot NHPh.$$

Pheneserine can be converted into dipheneserine by the further action of phenylcarbimide. If the above condensations are carried out in neutral solution in anhydrous ether and the first crop of crystals rapidly filtered off, these crystals are found to be *eseroline-phenylcarbimide*, $C_{13}H_{18}ON_2,PhCON$, m. p. 115—120°, which is very strongly alkaline, and is rapidly saponified by alkalis. It is readily converted into dipheneserine and pheneserine by shaking its ethereal solution with aqueous sodium hydroxide.

Geneseroline under similar conditions only gives one compound with phenylcarbimide, namely, *phenegeneserine*,

$$C_{13}H_{17}ON_2\cdot O\cdot CO\cdot NHPh,$$

m. p. 164°; $[\alpha]_D$ −125·5° in chloroform solution; it forms a *picrate*, m. p. 172°. When reduced with zinc and acetic acid, phenegeneserine is readily converted into pheneserine.

When eserine is condensed in neutral ethereal solution with phenylcarbimide an oily product is obtained. If the two substances are heated together, without a solvent, in the presence of a trace of sodium acetate in a sealed tube at 100° for two hours, from the product *dicarbanilidoeserine*, m. p. 100°, $[\alpha]_D$ −230°, can be isolated. Eserethol behaves similarly, giving an oily product, from which a little *dicarbanilidoeserethol*, $[\alpha]_D$ about −235°, is isolated.

Geneserine and generserethol do not react with phenylcarbimide.

W. G.

Scopoline. Ernst Schmidt (*Arch. Pharm.* 1916, **253**, 497—504).—Mainly an account of work already published (A., 1906, i, 104; 1909, i, 173). The methylpiperidinedicarboxylic acid obtained by the oxidation of hydroscopoline (*loc. cit.*) forms a *dimethyl* ester, the *methiodide*, $C_6H_{11}N(CO_2Me)_2,MeI$, of which, m. p. 175—176°, crystallises in anhydrous prisms (the corresponding *aurichloride*, $C_6H_{11}NMe[CO_2Me]_2,AuCl_4$, yellow crystals, has m. p. 124—125°). Although Willstätter and Lessing record 167—168° as the m. p. of the methiodide of methyl 1-methylpiperidine-2:6-dicarboxylate, the identity of the oxidation product of hydroscopoline with 1-methylpiperidine-2:6-dicarboxylic acid has been proved by direct comparison with the latter, synthetically prepared acid.

$$\begin{array}{l} CH_2\cdot CH\text{---}CH\cdot OH \\ CH_2\ \ NMe\ \ \ \ | \\ CH_2\cdot CH\text{---}CH\cdot OH \end{array}$$

Hydroscopoline, therefore, has very probably the annexed formula.

C. S.

Degradation of Scopoline. Scopoline ⟶ Hydroscopoline ⟶ Scopolic Acid. Kurt Hess and A. Suchier (*Ber.*, 1915, **48**, 2057—2067. Compare this vol., i, 74).—The present knowledge of the constitution of scopoline may be summed up in the scheme $C_8H_{13}O_2N = C_7H_9,NMe,OH,O\colon$. The authors have now attempted to throw some light on the constitution of the residue, C_7H_9, by

investigating the oxidation of scopoline and its derivatives, in the hope of obtaining amino-acids of cyclic bases which might be known. Scopoline itself was found to be unsuitable for such a purpose. It was therefore hoped that norscopoline would furnish a suitable amino-ketone on oxidation with formaldehyde (a new oxidation method, this vol., i, 67), but the base was merely reconverted into scopoline. This point will be discussed later, as it probably means that the hydroxyl group in scopoline is a tertiary one. Scopolyl chloride (Willstätter and Hedley, A., 1912, i, 577) was likewise unsuitable.

It has been found, however, that by heating scopoline with a solution of hydrogen bromide in glacial acetic acid at 115—120° in a sealed tube it gives the hydrobromide of an additive compound, which is easily reduced to a hydroscopoline by means of zinc and an acid. The latter base gives an acid on oxidation with chromic acid which is identical with the 1-methylpiperidine-2:6-dicarboxylic acid recently synthesised from lutidine (this vol., i, 74), and now designated *scopolic acid.* The positions of all the carbon atoms in scopoline are therefore revealed, and the alkaloid is proved to belong to the piperidine series.

The addition of hydrogen bromide in acetic acid gave two products, namely, the *hydrobromide* of the additive compound, $C_8H_{14}O_2NBr,HBr$, long, rectangular prisms, m. p. 210—211° (decomp.), and the corresponding hydrobromide of the *diacetate,* triclinic pyramids, m. p. 283—285° (decomp.), the latter being easily removed by reason of its ready solubility in methyl alcohol. The *hydroscopoline,* $C_8H_{15}O_2N$, formed indefinite crystals, quite unlike scopoline, m. p. 165°, reduced ammoniacal silver solutions, absorbed bromine readily, and yielded a *hydrobromide,* m. p. 260° (decomp.), a *picrate,* m. p. 232°, a very soluble *aurichloride,* m. p. 200°, and an extremely characteristic *double* salt with zinc bromide, $C_8H_{15}O_2N,HBr,\frac{1}{2}ZnBr_2$, which crystallised from glacial acetic acid in massive spikes, often a centimetre long, m. p. 215—216°.

J. C. W.

Yohimbine. III. Constitution of Yohimbine, and its Relationship to Yohimboaic Acid. Mesoyohimbine, a New Yohimbehe Alkaloid. L. Spiegel (*Ber.*, 1915, **48**, 2077—2083).—The researches and analyses published in earlier papers (compare A., 1904, i, 521) were regarded by the author as demonstrating that yohimbine is the *N*-methylated methyl ester of yohimboaic acid, that is, it differs by C_2H_4, thus, $C_{22}H_{28}O_3N_2$ and $C_{20}H_{24}O_3N_2$. Recently, however, Fourneau and Page (A., 1914, i, 862), who thought to have proved that yohimbine is identical with quebrachine (compare following abstract), suggested that the author's analyses might be interpreted in favour of $C_{21}H_{26}O_3N_2$, the accepted formula of quebrachine. The author now shows that Fourneau's own material contained a new ingredient, mesoyohimbine. Barger and Field, on the other hand (A., 1915, i, 835), agreed with the formula $C_{22}H_{28}O_3N_2$ for yohimbine, but proposed $C_{21}H_{26}O_3N_2$ for yohimboaic acid. The author points out that the

barium salt which these workers analysed is scarcely a trustworthy material for such a purpose.

Considerable light is now thrown on the subject by the isolation of an intermediate compound, $C_{21}H_{26}O_3N_2$, which should be called "noryohimbine," but as this name was originally given to yohimboaic acid, the new base is designated *mesoyohimbine*. It is met with in technical yohimbine, and can be isolated from this by crystallisation from 50% alcohol, in which it is the more soluble. It can be obtained from pure yohimbine by heating this with dilute alcoholic potassium hydroxide ($\frac{1}{2}$ mol.), and can be converted into yohimboaic acid on further hydrolysis. It crystallises in needles, m. p. 247° (yohimbine has m. p. 234·5°), is dextrorotatory, gives a crystalline hydrochloride, and contains a methoxyl group.

J. C. W.

Yohimbine. IV. The Supposed Identity of Yohimbine and Quebrachine. L. SPIEGEL (*Ber.*, 1915, **48**, 2084—2087. Compare Fourneau and Page, A., 1914, i, 862, and preceding abstract).—Fourneau and Page compared yohimbine with a specimen of "quebrachine" from Merck & Co., but the author has found that this preparation consists really of yohimbine and mesoyohimbine. Comparing the properties of yohimbine with those originally assigned by Hesse to his "quebrachine" (A., 1882, 742), it is doubtful whether Hesse's alkaloid was really yohimbine itself. Hesse, after examining what remains of his original preparation, inclines to the view that his "quebrachine" was yohimbine. Probably it was a mixture of related alkaloids. One thing is certain: that the alkaloid is only a casual constituent of *Quebracho blanco* (compare Ewins, T., 1914, **105**, 2738). J. C. W.

Relation between Absorption and Structure. II. Chromoisomerism and Chromotropy with Acid Additive Products of Aldamines. V. A. IZMAILSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1626—1643. Compare A., 1915, ii, 198).—The author advances the view that the cause of chromo-isomerism in the so-called cyclammonium (pyridinium, quinolinium, acridinium) salts is to be sought partly in the presence of azomethine groups. Attention is drawn to the structural similarity of the alkylideneamines or aldamines to the auramines and the so-called pyridine colouring matters, and the conclusion drawn that the simplest azomethine compounds may be obtainable in chromoisomeric and chromotropic forms. This conclusion is confirmed experimentally. Further, modification is required of Decker and Remfry's view (A., 1909, i, 408) that existence in differently coloured forms is confined to those "ammonium" salts, particularly the iodides, in which the nitrogen belongs to the ring, since this phenomenon is observed also in cases where the nitrogen belongs to an azomethinic group of an open chain. These salts exhibit the following characteristics: in the existence of the differently coloured salts the temperature and the solvent play an important part; the colour of the salt depends largely on the

anion; when treated with alkali, the salts form carbinols or pseudobases, which readily lose water and are converted into anhydrobases. The latter decompose more or less readily into carbonyl and amine components, the simplest members of this class being sensitive to traces of water or alcohol. The sensitiveness towards water may be diminished considerably by intensifying the basic properties of the chromo-radicles, for instance, by introduction of the amino-group. The only solvent with the help of which the two forms are obtainable is acetic anhydride, and in most cases only a mixture of the two is formed; the more intensely coloured modification is always the more soluble.

Special consideration is given to the case of benzylideneaniline, which exhibits isomeric additive products. With aldamines containing an auxochrome group in the para- or ortho-position to the azomethine group there may be quinonoid re-grouping, but with benzylideneaniline the only possible interpretation is that the chromoisomerism is similar to that of triphenylcarbinol salts. The anhydro-bases of a number of analogous compounds were investigated. The parallelism to triphenylmethyl salts is emphasised by the ability of certain of these bromides and iodides to form with stannic bromide and iodide strongly absorbent salts.

The chromoisomerism of the so-called pyridine dyes should undoubtedly be considered from the same point of view (compare König, A., 1913, i, 1082), since such dyes represent amino-substituted alkylideneimines and belong, therefore, to the group of azomethine salts. To the latter are related also the auramines, with which it is possible to obtain additive products in chromoisomeric forms (compare Semper, A., 1913, i, 577; Graebe, A., 1902, i, 683). With various carbonylic compounds, such as distyryl ketone, the additive products exist in colourless and also coloured forms. Chromoisomeric additive products are found also with azo-compounds, *p*-aminoazobenzene, for example, giving two hydrochlorides.

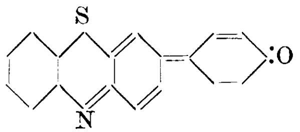
As regards the nomenclature of the adducts, the author prefers the name "hydrogenochloride," etc., to "hydrochloride," etc., of an amine or imine, the latter being suitable in cases where the formation of the additive product is accompanied by scission of water.

The hydrogen–iodide additive products of benzylideneaniline exist in the three chromotropic forms: (1) dark red needles, decomposing at about 157°; (2) orange, hexagonal plates, which may possibly be mixed crystals of (1) and (3); (3) yellow leaflets or scales. Additive products of benzylidene-*p*-iodoaniline, benzylidene-β-naphthylamine, cinnamylidenephenylamine, and diphenylmethylidenephenylamine (also termed phenyliminobenzophenone, benzophenoneanilide, etc.) are also considered. The last of these compounds forms a hydrogenobromide, which gives a dark red solution with stannic bromide. T. H. P.

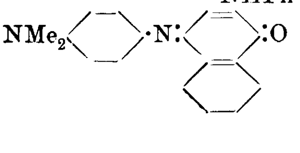
Preparation of Indole. W. GLUUD (D.R.-P. 278282; from *J. Soc. Chem. Ind.*, 1916, **35**, 106).—The elimination of carbon dioxide and water from *o*-aldehydophenylglycine by warming with

acetic anhydride, preferably with the addition of fused sodium acetate, results in the formation of indole. G. F. M.

Oxidation of Thiodiphenylamine. L. PESCI (*Gazzetta*, 1916, **46**, i, 103—118).—Oxidation of thiodiphenylamine by means of mercury acetamide (compare Forster, T., 1898, **73**, 793) proceeds according to the equation: $2S<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>NH + Hg(NHAc)_2 = Hg + 2NH_2Ac + S<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>N\cdot N<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>S$; a similar oxidation is effected by means of yellow mercuric oxide. o-*Dithiotetraphenylhydrazine*, $C_{24}H_{16}N_2S_2$, thus obtained, forms an almost white, amorphous powder, and decomposes without melting; it remains unchanged when treated with zinc and acetic acid, and, like tetraphenylhydrazine, it does not reduce Fehling's solution. In concentrated sulphuric acid it gives a red solution which turns green on addition of a small proportion of a nitrate or nitrite, but with ethereal hydrochloric acid it gives no coloration (compare Wieland and Gambarjan, A., 1906, i, 453).



o:o-*Thiodiphenoquinoneanil* (annexed formula), obtained, together with dithiotetraphenylhydrazine, etc., when a mixture of thiodiphenylamine and aniline is oxidised by means of yellow mercuric oxide, forms shining, reddish-yellow laminæ with metallic lustre, m. p. 150°. Its *hydrochloride*, $C_{18}H_{11}ONS,HCl$, forms dark green needles with metallic lustre, and, in hot aqueous solution, dyes wool and silk a bright bluish-green, which withstands washing with water and is changed to violet-red by the action of a base. The *zincichloride*, $(C_{18}H_{11}ONS,HCl)_2,ZnCl_2$, forms dark green needles with the lustre of copper. Reduction of the base by means of ammonium sulphide in pyridine solution yields the *leuco*-base, $C_{18}H_{13}ONS$, which is obtained in pale red crystals and is rapidly oxidised in the air, especially in presence of moisture or ammonia or potassium hydroxide solution. The *anilide* of the base, $C_{24}H_{16}ON_2S$, crystallises in small, cantharides-green laminæ, m. p. 215°, and forms an *acetate*, $C_{24}H_{16}ON_2S,C_2H_4O_2$, m. p. 127°, and a *hydrochloride*, $C_{24}H_{16}ON_2S,HCl$, which decomposes without melting. The action of methyl iodide on the anilide in methyl-alcoholic solution yields the *compound*, $C_{25}H_{18}ON_2S$, which crystallises in shining, cantharides-green needles, decomposing at about 210°; by ammonium sulphide in acetone solution it is converted into the *leuco*-base, $C_{24}H_{18}ON_2S$, which forms straw-yellow needles, turning brown at about 200°, m. p. 225°, and oxidises rapidly in moist air.



Indophenol also yields an *anilide* (annexed formula), which crystallises in rhombohedra or needles, m. p. 196—197°, and forms violet-blue solutions in acetone, pyridine, ether, alcohol, or light petroleum; the *hydrochloride*,

$C_{24}H_{21}ON_3,2HCl$,

was prepared. Hydrolysis of the anilide by means of hydrochloric acid in the cold yields 2-anilinonaphthaquinone and *p*-aminodimethylaniline, whilst in the hot *p*-aminodimethylaniline, aniline, and 2-hydroxynaphthaquinone are formed. T. H. P.

Reduction of Indigotin by means of Triethylphosphine. N. Kishner (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2129—2132).—Indigotin, which is stable towards oxygen, is oxidised by the latter in presence of triethylphosphine, this being converted into the unstable triethylphosphine peroxide, $PEt_3<\overset{O}{\underset{O}{|}}$; the indigotin then takes part of the oxygen of this peroxide, which is transformed into the corresponding oxide. Triethylphosphine also exerts, however, a reducing action on indigotinsulphonic acid, which it converts into the white leuco-compound. This reduction proceeds even in presence of atmospheric oxygen, and precedes the oxidation referred to above. It is expressed by the equations:

$$C_6H_4<\begin{matrix}CO\\NH\end{matrix}>C:C<\begin{matrix}CO\\NH\end{matrix}>C_6H_4 + 2H_2O \longrightarrow$$

$$C_6H_4<\begin{matrix}C(OH)_2\\NH\end{matrix}>C:C<\begin{matrix}C(OH)_2\\NH\end{matrix}>C_6H_4 + PEt_3 \longrightarrow$$

$$C_6H_4<\begin{matrix}C(OH)\\NH\end{matrix}>C\cdot C<\begin{matrix}C(OH)\\NH\end{matrix}>C_6H_4 + PEt_3(OH)_2 \longrightarrow PEt_3O + H_2O;$$

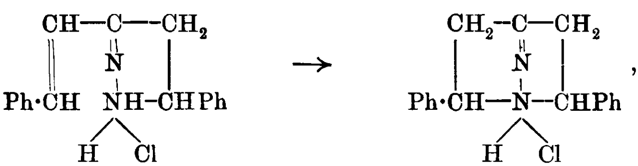
it may be carried out so as to serve as a striking lecture experiment.
T. H. P.

Action of Hydrazine on Dibenzylideneacetone [Distyryl Ketone]. Conversion into Derivatives of *cyclo*Propane and *cyclo*Pentane. N. Kishner (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1819—1848).—The structural similarity between phorone and distyryl ketone suggests the possibility of converting the latter, by the action of hydrazine, into a pyrazoline derivative capable of decomposing into nitrogen and a derivative of *cyclo*propane (compare A., 1913, i, 1163); this expectation is not, however, confirmed experimentally. The nature of the final product obtained varies with the proportions of the reacting compounds: (1) when not more than 1 mol. of hydrazine is used per mol. of distyryl ketone, 5-phenyl-3-styrylpyrazoline, $CHPh:CH\cdot C<\begin{matrix}CH_2\cdot CHPh\\N\text{---}NH\end{matrix}$, is formed; (2) when, however, excess of hydrazine is present, 2 molecules of the above pyrazoline base unite with 1 molecule of hydrazine, giving the compound $\left(\begin{matrix}CHPh\cdot CH_2\\NH\text{——}N\end{matrix}>C\cdot CH_2\cdot CHPh\cdot NH\cdot\right)_2$, (I), the formation of which is completely analogous to the union of hydroxylamine with distyryl ketoneoxime at the double linking. When heated, 5-phenyl-3-styrylpyrazoline decomposes, without the intervention of a catalyst, giving 3 : 4-diphenyl*cyclo*pentene,

$\begin{array}{l}CHPh\cdot CH_2\\ |\\ CHPh-CH\end{array}\!\!>\!CH$. When heated with hydrochloric acid, compound (I) (*vide supra*) yields the hydrochlorides of hydrazine and 5-phenyl-3-styrylpyrazoline, but when heated alone it decomposes in two directions: (1) part gives hydrazine and 5-phenyl-3-styrylpyrazoline, the latter then undergoing change into nitrogen and 3:4-diphenyl*cyclo*pentene; (2) the other part undergoes scission at the hydrazine residue, losing nitrogen and giving 5-phenyl-3-β-phenylethylpyrazoline, $CH_2Ph\cdot CH_2\cdot C\!\!<\!\!\begin{array}{l}CH_2\cdot CHPh\\ N\!-\!\!-\!NH\end{array}$; this compound, when heated in presence of potassium hydroxide and platinised porous tile, loses nitrogen, forming 1-phenyl-2-β-phenylethyl*cyclo*propane.

The *compound*, $C_{34}H_{36}N_6$, formula (I), forms white, acicular crystals, m. p. 55—60°, and could not be recrystallised on account of its instability; in a vacuum over sulphuric acid it may be kept for a long time unchanged.

5-*Phenyl*-3-*styrylpyrazoline*, $C_{17}H_{16}N_2$, forms lemon-yellow, acicular crystals, m. p. 77—78° (decomp.). Its *hydrochloride*, $C_{17}H_{16}N_2,HCl$, forms elongated, hexagonal, yellow plates, m. p. 169—170° (decomp.), and its 1-*nitroso*-derivative forms pale yellow needles, m. p. 151°, and forms a compound, $(C_{17}H_{15}ON_3)_2,C_6H_6$, in golden-yellow needles. With phenylthiocarbimide it gives the *compound*, $C_{24}H_{21}N_3S$, m. p. 160·5°. When the hydrochloride is heated, loss of hydrogen chloride is accompanied by isomerisation of the free base into the dipyrazoline base:



the formation of the second pyrazoline ring being essentially similar to the formation of the first ring in the action of hydrazine on distyryl ketone. The *dipyrazoline base* forms rectangular plates, m. p. 97·5°, b. p. 255°/10 mm., or 424°/737 mm., and exhibits only feeble basic properties; in acetic acid its cryoscopic behaviour is normal, but in freezing benzene the molecular weight increases from 416 (1·42% solution) to 594 (5·47%), the value 496 corresponding with the doubled formula; its *hydrochloride*, m. p. 202—204°, was prepared.

3:4-*Diphenyl*cyclo*pentene*, $C_{17}H_{16}$, is a colourless, odourless liquid, b. p. 321·5°/747 mm., D_4^{20} 1·0360, n_D^{20} 1·5881, and is rapidly oxidised by permanganate in the cold. 3:4-*Dibromo*-1:2-*diphenyl*cyclo*pentane*, $C_{17}H_{16}Br_2$, forms colourless, rhombic plates, m. p. 119°, has the normal molecular weight in freezing benzene, and is converted by zinc dust and alcohol into 3:4-diphenyl*cyclo*pentene; the latter is therefore more simply obtained by means of this dibromo-derivative, the preparation of 5-phenyl-3-styrylpyrazoline in the pure state being avoided. Oxidation of 3:4-diphenyl*cyclo*pentene by

potassium permanganate yields benzoic and $\alpha\beta$-diphenylglutaric acids. The latter acid (compare Avery and McDole, A., 1908, i, 343; Borsche, A., 1910, i, 35) exists in (1) a maleinoid modification, m. p. 200—201°, which forms a *methyl* ester, m. p. 87°, and an *ethyl* ester, m. p. 75—76°, and (2) a fumaroid form, m. p. 220—221°, which gives a *methyl* ester, m. p. 140·5°, and an *ethyl* ester, m. p. 95—96°. In ethereal solution and in presence of platinum-black, 3:4-diphenyl*cyclo*pentene readily undergoes hydrogenation to 1:2-diphenyl*cyclo*pentane, m. p. 65·5°, b. p. 321·5°/735 mm., identical with the hydrocarbon obtained by reducing diphenyl*cyclo*butylidenemethane with hydrogen iodide (compare Kishner, A., 1911, i, 43).

5-*Phenyl*-3-β-*phenylethylpyrazoline*, $C_{17}H_{18}N_2$, is a colourless, viscous liquid, b. p. 222°/10 mm., D_4^{20} 1·0625, n_D^{20} 1·5874, and forms a viscous *hydrochloride*, which turns violet in the air.

1-*Phenyl*-2-β-*phenylethyl*cyclo*propane*, $CH_2<\begin{matrix}CHPh\\|\\CH\cdot CH_2\cdot CH_2Ph\end{matrix}$, is a colourless, odourless liquid, b. p. 204·5°/28 mm., D_4^{15} 0·9995, n_D^{15} 1·5666, optical exaltation 0·84; it exhibits a saturated character towards permanganate, and in chloroform solution combines slowly with bromine. With hydrogen bromide it gives a compound which, when boiled with aqueous alcoholic potassium hydroxide, yields an unsaturated hydrocarbon, probably $\alpha\epsilon$-*diphenyl*-Δ^β-*pentene*, $CH_2Ph\cdot CH:CH\cdot CH_2\cdot CH_2Ph$, b. p. 328°/746 mm., 180°/18 mm., 172°/8 mm., D_4^{20} 1·0226, n_D^{20} 1·5872; this hydrocarbon is oxidised by permanganate, and combines with two atoms of bromine.

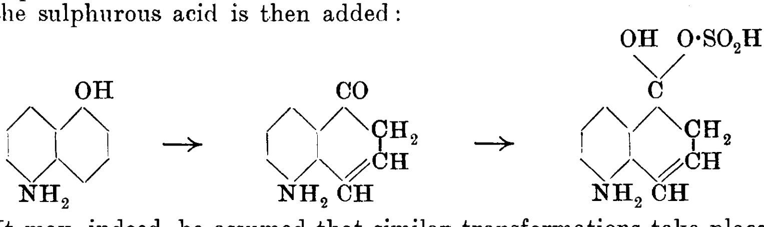
T. H. P.

Behaviour of Certain Metallic Oxides towards Phenylhydrazine. ERNESTO PUXEDDU (*Gazzetta*, 1916, **46**, i, 71—76).—In the absence of solvent, the various oxides of mercury react vigorously with phenylhydrazine, with marked rise of temperature; the action is less energetic with the red, crystalline oxide or with old yellow oxide than with freshly prepared yellow oxide, but when finely powdered the red oxide reacts immediately. Yellow or red mercuric oxide is reduced by phenylhydrazine in ethereal solution, the mercury being precipitated in a bluish-grey, pulverulent form, and mercury diphenyl formed (compare Fischer, A., 1880, 234). In one instance, a sample of the yellow oxide which had been prepared some months gave, with ethereal phenylhydrazine, the pulverulent mercury mixed with a white compound, forming nacreous scales, m. p. about 250°. Mercurous oxide is also energetically reduced to mercury by phenylhydrazine. Lead peroxide reacts instantaneously and vigorously with phenylhydrazine, yielding lead and its oxide and suboxide. Triplumbic tetroxide reacts with phenylhydrazine when gently heated, the resulting products being similar to those obtained with lead peroxide. T. H. P.

Reducing Properties of Phenylhydrazine. ERNESTO PUXEDDU (*Gazzetta*, 1916, **46**, i, 62—70).—The author gives a summary of the literature referring to phenylhydrazine as a reducing agent, and

describes the results obtained by himself by the reduction in this way (1) of various metallic oxides (preceding abstract), and (2) of bisazo-compounds, with the view of showing that the latter may give rise to either diaminophenols or aminohydroxyazo-compounds, according to the extent to which the reduction proceeds. With bisazocarvacrol the reduction is complete, the product being diaminocarvacrol [OH : Me : Pr : $(NH_2)_2=2:1:4:3:5$], which is a highly unstable compound and is easily transformed by concentrated ferric chloride solution into hydroxythymoquinone; bisazothymol behaves similarly. Other bisazo-compounds, prepared according to Nölting and Kohn's indications (A., 1884, 900), give, however, under certain conditions, compounds which appear to be amino-hydroxyazo-compounds, and are under investigation. Phenyl-hydrazine also reduces azo-derivatives of aromatic hydroxy-aldehydes, the azo-group being reduced as with the hydroxyazo-compounds, except that the presence of the aldehyde group leads to the formation of the hydrazone. Thus, the azo-derivative of salicyl-aldehyde yields 5-amino-2-hydroxybenzaldehydephenylhydrazone. The advantages of phenylhydrazine as a reducing agent for hydroxyazo-compounds are: (1) the rapidity of the action, either in the cold or with gentle heating; (2) the amino-compound may often be separated in crystals by addition to the products of the reaction of a suitable solvent; (3) good yields of highly pure products; and (4) the general character of the reaction. T. H. P.

Bisulphite Compounds of Hydroxyazo-colouring Matters. II. N. N. Voroshcov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1669—1737, Compare A., 1911, i, 819).—The compounds obtained by the action of sodium hydrogen sulphite on sodium 1:5- and 1:8-naphthol-sulphonates represent anhydrous esters, $SO_2Na\cdot O\cdot C_{10}H_6\cdot SO_3Na$, whereas those obtained from 1:5- and 1:8-aminonaphthols, which are separable only with the hydrogen unsubstituted, and not as salts, contain an extra molecule of water, $NH_2\cdot C_{10}H_6\cdot OH + H_2SO_3$. The stability of the latter compounds indicates that this molecule of water is constitutional, and the conclusion is drawn that the naphtholic nucleus is first converted into the ketonic form, to which the sulphurous acid is then added:



It may, indeed, be assumed that similar transformations take place with the naphtholsulphonates, the products thus formed then losing 1 mol. of water. There is no reason to expect that diazotisation should produce any change in the ring not containing the amino-group, and this is confirmed by analysis of the compound obtained by coupling the diazotised sodium hydrogen sulphite derivative of 1:5-aminonaphthol with phenol, the final product still containing

the additional molecule of water; thus, such colouring matters cannot have the ordinary ester structures assigned to them by Bucherer (A., 1904, i, 309; 1905, i, 48) and others (compare Lebedev, *Diss.*, *Dresden*, 1914).

α-Naphthylamineazo-2-aminobenzoic acid yields the same compound with sodium hydrogen sulphite as does α-naphtholazo-2-aminobenzoic acid, the resulting colouring matter having after hydrolysis a hydroxyl group in its naphthalene component. Similar replacement of the amino-group by hydroxyl takes place in the action of sodium hydrogen sulphite on β-naphthylamineazo-4-aminobenzenesulphonic acid and on *p*-aminophenol-azo-β-naphthylamine.

The structure given above for the compounds obtained by the action of sodium hydrogen sulphite is confirmed in a number of other cases.

[With A. Domke.]—The sodium hydrogen sulphite *compound* of 1:4-naphtholsulphonic acid, $C_6H_4<\begin{matrix}C(OH)(O\cdot SO_2Na)\cdot CH_2 \\ C(SO_3Na)=\!=\!=\!=\!=CH\end{matrix}$, forms colourless, hygroscopic crystals, but was not obtained free from mineral salt.

Descriptions are given of the compounds obtained by treatment of 1:5- and 1:8-aminonaphthols with sodium hydrogen sulphite, followed by diazotisation and coupling with phenol or α- or β-naphthol.

[With A. Portner.]—The relations towards sodium hydrogen sulphite of azo-colouring matters derived from the three diazotised monosulphonic acids of aniline and the monoamino- or monohydroxy-derivative of naphthalene:

$$SO_3H\cdot C_6H_4\cdot N{:}N\cdot C_{10}H_6\cdot Aux(OH \text{ or } NH_2).$$

The cases investigated comprise: SO_3H in the ortho-position; Aux in the (1) α-, (2) β-position; SO_3H in the meta-position, Aux in the (3) α-, (4) β-position; SO_3H in the para-position, Aux in the (5) α-, (6) β-position. (Aux = auxochrome.)

[With I. Aronschtam.]—Similarly, the behaviour towards sodium hydrogen sulphite of the twelve azo-colouring matters represented by the scheme $CO_2H\cdot C_6H_4\cdot N{:}N\cdot C_{10}H_6\cdot Aux(OH \text{ or } NH_2)$ has been studied.

[With St. Ratschinski.]—Similar investigations have been made on the colouring matters derived from diazotised *p*-aminophenol and α- or β-amino- or hydroxy-naphthalene.

The action of sodium hydrogen sulphite on α-naphtholbisazobenzene, 1-naphthol-2-azobenzene, and 1-naphthol-2-azobenzene-4-sulphonic acid has also been studied.

When treated with sodium hydrogen sulphite, *p*-dimethylaminoazobenzene, *p*-diethylaminoazobenzene, and *p*-nitrobenzenediazodiphenylamine first undergo scission. In the case of 1-benzeneazo-4-methoxynaphthalene, the methoxy-group is replaced by hydroxyl.

T. H. P.

Non-aromatic Diazonium Salts. V. Diazo-derivatives of Aminotriazoles. Gilbert T. Morgan and Joseph Reilly (T., 1916, **109**, 155—160).—Thiele and Manchot (A., 1899, i, 167)

found that aminotriazoles in hydrochloric acid solution yield diazonium salts which couple with bases like β-naphthylamine. They noticed, however, that the diazo-compounds are very unstable in the presence of hydrochloric acid, the diazo-nitrogen being evolved, with the production of chlorotriazoles. The present authors have found that the diazo-compounds are stable, however, in the presence of an oxy-acid, and have obtained characteristic derivatives of them.

5-Amino-3-methyl-1 : 2 : 4-triazole was prepared from aminoguanidine nitrate through the acetylaminoguanidine nitrate, and treated with sodium nitrite in the presence of dilute nitric acid. The diazo-compound was isolated as 5-*diazo*-3-*methyl*-1 : 2 : 4-*triazole aurichloride*, $C_3H_3N_5,H_2O,AuCl_3$, a heavy precipitate of rosettes of small, bright yellow prisms, and condensed with alcoholic β-naphthol to form 3-*methyl*-1 : 2 : 4-*triazole*-5-*azo*-β-*naphthol*, $C_{13}H_{11}ON_5$, dark orange-brown plates and flattened needles, m. p. 213—215°. When a solution of the diazonium nitrate, obtained by the action of ethyl nitrite, is evaporated to dryness over potassium hydroxide at the ordinary temperature, 3-*methyl*-1 : 2 : 4-*triazole*-5-iso*diazohydroxide* is obtained as a colourless residue which crystallises from alcohol in prismatic needles, $C_3H_5ON_5,EtOH$. This does not couple with β-naphthol unless it is first dissolved in moderately concentrated nitric or sulphuric acid.

5-Amino-1 : 2 : 4-triazole was obtained from formylaminoguanidine nitrate and diazotised as above. 5-*Diazo*-1 : 2 : 4-*triazole aurichloride*, $C_2HN_5,AuCl_3$, forms opaque, yellow granules; 1 : 2 : 4-*triazole*-5-*azo*-β-*naphthol*, $C_{12}H_9ON_5$, forms acicular, orange crystals, m. p. 252—255°; 1 : 2 : 4-*triazole*-5-*azo*-β-*naphthylamine* crystallises in dark brownish-red plates, m. p. 243—245°. 1 : 2 : 4-*Triazole*-5-iso*diazohydroxide* was not isolated in as pure a condition as the homologue.

The above azo-dyes are soluble in dilute potassium hydroxide, which is doubtless due to the imino-group in the triazole ring.

J. C. W.

Composition and Properties of Nutrose. M. A. Rakuzin and (Mlle.) Ek. Maks. Braudo (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1852—1853).—"Nutrose" is sold as a tasteless powder neutral to phenolphthalein, and, like casein, shows all the colour reactions of the proteins with the exception of Liebermann's reaction. It has $[\alpha]_D$ −145·45°, and its ash-content (Na_2CO_3) is 4·63%. All these properties are in agreement with those of sodium caseinate. The method employed to manufacture this preparation in large quantities and in the form of a powder remains a secret. The authors have prepared a number of coloured caseinates with salts of the heavy metals.

T. H. P.

The Influence of Temperature and Poisons on Enzyme Action, Fermentation, and Growth. Otto Rahn (*Biochem. Zeitsch.*, 1916, **72**, 351—377).—A theoretical paper, in which Tammann's theory of enzyme action is applied to explain various actions of ferments and poisons. Two main actions in the case of the

enzymes are considered, namely, the action of the enzyme on the substrate, and the rate of destruction of the enzyme. The equations for a unimolecular reaction, and the equation of Arrhenius connecting the reaction constant with the temperature, are applied. The conclusions drawn in the case of the action of emulsin are as follows: The action of the ferment on the substrate has a normal temperature-coefficient; the higher the temperature, the greater the activity. At the higher temperatures, however, the amount of enzyme rapidly diminishes, and the increased activity acts in opposition to the destruction of the ferment. The rate of change of the latter process is greater than its increased activity with rise of temperature. At high temperatures it is therefore possible to observe a great initial rate of action, which after a few minutes, or even seconds, comes to a standstill. There is no "optimal" temperature for ferment action. Ferment actions are, generally, incomplete actions, which can approach completion at the lower temperatures, and the end-point recedes with higher temperatures. In a fermentation system (for example, with yeast cells) the enzymes are inside the cells as well as outside. The living cell, however, produces continually new quantities of enzyme to replace those destroyed. As the temperature-coefficient of cell destruction is high, a point is reached at which the part destroyed is no longer replaced entirely by that newly formed. As a consequence, the rate of fermentation, which at the start is very rapid, quickly falls off. In fermentation produced by a living cell there is true optimal temperature, and it is that at which the rate of production of new enzyme quantities is equal to the rate of destruction. Similar considerations can be applied to growth.

Poisons accelerate both the rate of action and rate of destruction of ferments. The actions can be subjected to a theoretical treatment similar to that applied to the consideration of the influence of temperature. S. B. S.

The Hydrolysis of Vegetable Proteins by Papain. N. T. DELEANU (*Bull. Sci. Acad. Roumaine*, 1915–1916, **4**, 207—216).—Various vegetable proteins when heated rapidly with papain are hydrolysed, and yield proteose, peptones, and amino-acids. Some of the proteins can be degraded into amino-acids at any temperature, whereas in the case of others the hydrolysis only takes place at medium temperatures not exceeding 45°. Coagulated proteins are attacked with greater difficulty than the uncoagulated; but the products of degradation are the same in both cases. Animal proteins, either coagulated or dried, are not attacked by papain. The proteins of seeds of lupines, when treated with papain, do not yield arginine, as they do on autolysis or germination. S. B. S.

Enzymes. X. Attempts to Synthesise Disaccharides by means of Enzymes. WALTHER LÖB (*Biochem. Zeitsch.*, 1916, **72**, 392—415).—An account is given of numerous attempts to synthesise sucrose from hexoses by means of invertase obtained from sugar beet, yeast, pancreas, and kephir. Under the conditions

of the experiments selected, no evidence of synthetic action of the ferment could be obtained. S. B. S.

Preparation of a Hexa-aminoarsenobenzene. C. F. BOEHRINGER & SÖHNE (D.R.-P. 286854 and 286855; from *J. Soc. Chem. Ind.*, 1916, **35**, 142).—3:5-Dinitro-4-aminophenylarsinic acid is reduced to the corresponding triamino-compound with the calculated amount of sodium hyposulphite, and this is further reduced with hypophosphorous acid to 3:4:5:3′:4′:5′-hexa-aminoarsenobenzene, or the operations may be reversed in order, with the intermediate production of a nitroarsenobenzene. In the second patent, 3:5-dinitro-4-aminophenylarsinic acid is reduced in one operation with a quantity of sodium hyposulphite sufficient to reduce both the nitro-groups and the arsinic acid group, and the resulting sulphur-containing compound, on decomposition with acids, yields sulphur dioxide and a salt of hexa-aminoarsenobenzene. This compound is characterised by its slight toxicity, and has valuable therapeutic properties on account of its powerful spirillocidal action.

G. F. M.

Preparation of a Tetra-aminodimethylaminoarsenobenzene. C. F. BOEHRINGER & SÖHNE (D.R.-P. 286667 and 286668, additions to D.R.-P. 285572, see A., 1914, i, 1101; from *J. Soc. Chem. Ind.*, 1916, **35**, 141—142).—Instead of using tin and hydrochloric acid for the reduction of dinitromethylnitroaminophenylarsinic acid, as prescribed in the chief patent, stannous chloride with hydrochloric acid or with hydrochloric and acetic acids, zinc with concentrated hydrochloric or acetic acid, or iron and hydrochloric acid may be used. To avoid formation of arsine, the reaction mixture is heated only until a clear solution is obtained. Reduction of the above nitro-arsinic acid may also be effected in stages; thus, reduction of 3:5-dinitro-4-methylaminophenylarsinic acid is brought about by mercury and sulphuric acid, and sodium hyposulphite further reduces this to tetra-aminodimethylaminoarsenobenzene. On the other hand, tetra-aminodimethylhydrazinoarsenobenzene may be first formed (this vol., i, 175) and then further reduced, or reduction may be effected by means of phosphorus or hypophosphorous acid to tetra-nitrodimethylaminoarsenobenzene, and this subsequently reduced to the tetra-amino-compound with tin and hydrochloric acid.

G. F. M.

Physiological Chemistry.

The Inhibitory Action of the Light of the Quartz Lamp on the Coagulation of Blood. WALTHER HAUSMANN and ERNST MAYERHOFER (*Biochem. Zeitsch.*, 1916, **72**, 379—382).—Plasma produced from blood rendered uncoagulable by the addition of a concentrated solution of sodium chloride will not coagulate on

addition of distilled water after it has been exposed to the rays of a quartz mercury lamp. Without such exposure, dilution causes coagulation in a few minutes; but this can be delayed by exposure to the rays after it has once commenced. Oxalate plasma coagulates after addition of calcium salts much more slowly if it has been exposed than does unexposed plasma. Attention is directed to the clinical importance of these results. S. B. S.

Influence of Salts on the Amylolysis of Bread. JEAN EFFRONT (*Mon. Sci.*, 1916, [v], **6**, 5—12).—The action of the saliva consists mainly in the rendering soluble of the starch during the first hour of the gastric digestion. This action of saliva on pure starch is very rapidly checked by the presence of hydrochloric acid in the gastric juice. The amylaceous substances of bread show, however, a much greater resistance to the acid than pure starch, this tolerance being due chiefly to the presence of phosphates in the bread. In whole-meal bread there is sufficient phosphate present to compensate for the acid accumulated during the first phase of digestion, and thus the starchy substances are rendered soluble. White bread is much less rich in phosphates, and its digestion is in consequence more difficult. There is more than one factor concerned in the action of the phosphates. The tri- and di-metallic phosphates contained in the bread partly neutralise the free hydrochloric acid, and the dihydrogen phosphate thus formed exerts a direct influence on the amylolytic enzyme of the saliva, making it more resistant to free acid. The dihydrogen phosphate also favours the peptonisation, and this good peptonisation has an indirect influence on the amylolysis. W. G.

Kephalin of the Egg Yolk, Kidney, and Liver. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1916, **24**, 111—116. Compare this vol., i, 199).—Specimens of kephalin obtained from commercial egg-yolk powder, from commercial lecithin, from kidney and liver, have the same composition as kephalin prepared from brain. Contrary to expectation, the authors have found that kephalin is extracted with less difficulty from the brain than from the other materials examined. H. W. B.

Nervous Tissues. I. Chemical and Physico-chemical Properties of Nerve Juice. F. BOTTAZZI and A. CRAIFALEANU (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 73—79).—The authors have examined the chemical composition and the physico-chemical properties of the juice obtained by triturating the nerve substance of ox-brain with quartz sand, mixing the resultant paste with kieselguhr and pressing under a pressure of 300 atmos. With the juice of the grey matter, the refractive index, viscosity, surface tension, and proportions of nitrogen and phosphorus are greater, and the electrical conductivity, depression of the freezing point, dry residue, specific gravity, and hydrogen-ion concentration less, than with the juice from the white matter. The former juice resembles blood-serum more than the latter does, probably owing, at least partly,

to the presence of more blood. The difference between the indices of refraction and viscosities of the two juices seems to depend on the difference between the nitrogen-contents. T. H. P.

Is Autolysis an Autocatalytic Phenomenon? MAX MORSE (*J. Biol. Chem.*, 1916, **24**, 163—167).—The author measures the rate of production of acid during the autolysis of an extract of thymus by Sörensen's method. The increase in the acidity runs parallel to the rate of autolytic digestion, and when the acid production reaches a maximum, digestion likewise reaches its maximum. Autolysis is therefore an autocatalytic phenomenon, the products of digestion entering into the reaction as true catalysts. H. W. B.

Enzymic Scission of Polypeptides by Means of Animal Tissues and Organs. I. A. CLEMENTI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 183—188).—The livers of birds, reptiles, amphibia, fishes, and invertebrates (molluscs) contain enzymes capable of hydrolysing *dl*-leucylglycine. Such hydrolysis takes place according to the principle of the asymmetric action of peptidolytic enzymes on racemic polypeptides, which has been shown to hold quantitatively with the peptidolytic enzymes of mammifers (A., 1915, i, 854). T. H. P.

The Reversibility of the Formation of Urea in the Liver. B. C. P. JANSEN (*Arch. Néerland*, 1915, [iii B], **2**, 594—599).—The livers of five dogs, some having been starved for various periods and others well nourished, were perfused with bullock's blood, 1700—1900 c.c. being used in each case, to which was added from 200 to 600 c.c. of 0·9% saline solution containing about 8 grams of urea. In one case the bullock's blood was replaced by 300 c.c. of blood from the same dog and 850 c.c. of blood from another dog, which had been starved for two days. In two cases 300—350 mg. of lactic acid, dissolved in a little water, were added after about half-an-hour. Samples of 100 c.c. of blood were collected at intervals after the experiment, and the amount of urea present estimated. The urea content of the liver at the end of the experiment was also determined. In every experiment there was a slight drop in the urea content of the blood at first, followed by a rise to about the original content. At the same time there was a very marked rise in the percentage of urea in the liver due to the perfusion. The results are in accord with those of Wakeman and Dakin (compare A., 1911, ii, 629), and show that, although the amount of urea in the blood was ten times the normal content, there was no destruction of urea in the liver, but rather the contrary. The addition of a small amount of lactic acid made no difference. The formation of urea in the liver is therefore apparently not a reversible reaction. The amount of ammonia in the perfusion liquid at the end of the experiment was very low (1—2 mg. per 100 c.c.) (compare Wakeman and Dakin, *loc. cit.*). W. G.

Does the Pituitary Gland Contain Adrenaline or a Compound Similar to it? WALTER K. WATANABE and ALBERT C. CRAWFORD (*J. Pharm. Expt. Ther.*, 1916, **8**, 75—88).—Pituitary extracts, when prepared by certain methods, are found to yield colour reactions which suggest the presence of adrenaline or a similar compound, and the physiological actions of such solutions can be explained by the assumption of the presence of adrenaline, but admixed with other substances. Adrenaline has not been isolated from these glands, but this may be due to the small amounts present, which might escape precipitation in the methods employed for obtaining adrenaline. H. W. B.

Lewis and Benedict Method for the Estimation of Blood Sugar, with Some Observations Obtained in Disease. VICTOR C. MYERS and CAMERON V. BAILEY (*J. Biol. Chem.*, 1916, **24**, 147—161. Compare Lewis and Benedict, A., 1915, ii, 111).—The Lewis-Benedict method may be simplified by employing an initial blood dilution of 1 : 5 instead of 1 : 12·5. In this way a sufficiently high concentration is obtained to obviate the necessity for evaporation in the development of the colour. For the colorimetric measurements, the Hellige colorimeter has been found especially satisfactory.

A number of cases of nephritis are reported with hyperglycæmias rising to 0·2 per cent. Nineteen advanced cases of diabetes were investigated, and it was found that the percentage output of dextrose in the urine compared with the dextrose in the blood in cases giving evidence of nephritis was considerably lower than in other cases of diabetes. One case is reported with 1·1 per cent. of dextrose in the blood and only 0·5 per cent. in the urine. Severe nephritis appears, therefore, to reduce markedly the permeability of the kidney for dextrose. H. W. B.

The Biological Method of Detection of the Proteinogenic Amines in Extracts of Organs and Tissue Fluids. M. GUGGENHEIM and WILLH. LÖFFLER (*Biochem. Zeitsch.*, 1916, **72**, 303—324).—The actions of various substances on the surviving small intestine of the guinea-pig were investigated. An apparatus is described and figured by means of which several experiments can be carried out at the same time, and the paper is illustrated by numerous tracings. The following were found to be the minimal doses which produce action when added to 100 c.c. of Ringer's solution: 0·000025 gram for β-amino-4-ethylglyoxaline, 0·001 gram for phenylethylamine hydrochloride and for *p*-hydroxyphenylethylamine; 0·005 gram for *iso*amylamine hydrochloride; 0·002 gram for indole-ethylamine hydrochloride; 0·00001 gram for adrenaline hydrochloride; 0·01 gram for methylguanidine nitrate; 0·01 gram for choline hydrobromide; 0·000001 gram for acetylcholine hydrobromide; and 0·001 gram for neurine hydrobromide. The following substances were active in doses of between 0·1 and 0·01 gram: the alkali salts of the higher fatty and bile acids, oxalates, and citrates, and in doses of 0·05—0·01 gram indole, phenol, cresol, guaiacol,

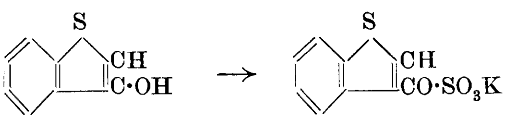
disodium hydrogen phosphate, and tyrosol. The following substances were inactive in doses of 0·1 gram per 100 c.c. of Ringer's fluid: aliphatic amino-acids, silk peptone, protein solutions, dihydroxyphenylalanine, histidine, tryptophan, *p*-hydroxyphenylacetic acid, homogentisic acid, methylamine and ethylamine hydrochlorides, trimethylamine hydrochloride, cadaverine, putrescine, guanidine, dextrose, lecithin. S. B. S.

The Fate of the Proteinogenic Amines in the Animal Body. M. GUGGENHEIM and WILH. LÖFFLER (*Biochem. Zeitsch.*, 1916, **72**, 325—350).—The following proteinogenic amines were investigated: *iso*amylamine, *p*-hydroxyphenylethylamine, indole-ethylamine, β-amino-4-ethylglyoxaline. They were rapidly rendered non-toxic in the organism owing to deamidising and oxidative processes. The end-products were carboxylic acids with the same number of carbon atoms as the base, namely, valeric, phenylacetic, *p*-hydroxyphenylacetic, and indoleacetic acids. The last-named acid was not definitely isolated, but its presence in the urine was shown to be probable. The acids are either excreted as such, or further altered in the organism. The alcohols, *iso*amyl, phenylethyl, and *p*-hydroxyphenyl alcohols, are intermediate products, which could be isolated when the amines were perfused through the liver. Furthermore, the mechanism suggested above for the degradation of the amines (amine–alcohol–acid) received further support from the fact that the alcohols also, when perfused through the liver, gave rise to the corresponding acids.

Normal blood and serum from man and animals (especially from rabbits) contain a substance which increases the tone of a surviving intestine of the guinea-pig; this is heat-stable and soluble in alcohol.

S. B. S.

The Behaviour of 3-Hydroxythionaphthen (Thioindoxyl) in the Organism. The Synthesis of Thioindican. ERWIN SCHWENK (*Biochem. Zeitsch.*, 1916, **72**, 383—391).—The behaviour of 3-hydroxythionaphthen in the organism is similar to that of indoxyl; it is excreted chiefly in the form of thioindican (annexed formula). It was also excreted in the form of a glycuronate. Thioindican was obtained synthetically by the action of chlorosulphonic acid on hydroxythionaphthen in pyridine solution. It melts (not sharply) at 225°, but commences to redden at 180°. In the presence of catalysts (such as ferric ammonium sulphate) it undergoes decomposition in the light.



(Thioindican.)

3-Hydroxythionaphthenglycuronate was also isolated from the urine of rabbits to which 3-hydroxythionaphthen was administered in the form of the salt $C_8H_5S{\cdot}O{\cdot}C_6H_8O_6K$, m. p. 199—200°.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Stability of Hypochlorites in Very Dilute Solutions. Consequences from the Point of View of their Use for the Sterilisation of Waters (Javelisation). LUCIEN VALLERY (*Compt. rend.*, 1916, **162**, 326—327).—In very dilute solutions, containing about 1 part of active chlorine in a million, hypochlorites undergo a very slow decomposition, which, according to the initial strength of the solution, may or may not be limited by an equilibrium, the limit being influenced in a marked manner by apparently very slight variations in the medium. This influence of the medium may be either a purely catalytic action, positive or negative, or a chemical action due to the presence in the medium of substances capable of reacting with the hypochlorites or their decomposition products. The action of germs in the water comes under one of these headings. Waters treated with hypochlorites in this way should not be used for drinking until the active chlorine present is less than 0·1 mg. per litre. The method should only be used for sterilising waters where it can be controlled by analysis.

W. G.

Boron: its Absorption and Distribution in Plants, and its Effect on Growth. F. C. COOK (*J. Agric. Research*, 1916, **5**, 877—890).—Pot experiments in which wheat, sugar beet, tomatoes, cowpeas, and lettuce were manured with borax and calcined colemanite (calcium borate); also plot experiments with soja beans, potatoes, maize, wheat, oats, peas, and other plants. Wheat, beans, cowpeas, and tomatoes contained boron chiefly in the tops of the plants and comparatively little, or none, in the roots. In the case of potatoes, the roots and tubers contained relatively large amounts of boron, whilst the leaves and stems contained only small amounts. The fruit of cowpeas contained large amounts of boron, and the fruit of tomatoes only traces. The yield of wheat manured with borax was 90% of the yield on the manured control plot, and higher than on the unmanured plot.

Leguminous plants take up the largest amounts of boron and are the most easily injured. The same amounts of boron have different effects in different soils: Addition of 0·0011% of boron to soil may be injurious to leguminous plants; with other plants this amount is neither injurious nor stimulating.

Boron is widely distributed in soil, and all the plants grown on control plots were found to contain some boron. N. H. J. M.

Oxydases. HERBERT H. BUNZELL (*J. Biol. Chem.*, 1916, **24**, 91—102).—The oxidation of certain aromatic substances, such as tyrosine, phloridzin, and pyrogallol, by oxygen in the presence of extracts of plant tissues ceases after a definite period, which ranges within wide limits according to the experimental conditions. The

abrupt ending of the influence of the plant material is due to the complete utilisation of the oxydase or other catalytic agent present, and can be postponed by the addition of a further quantity of the plant tissue. The extent of oxidation in each case is thus practically proportional to the quantity of active plant material used. The effects of shaking, of the reagents employed, and of the products formed, on the course of the oxidation have been studied, as well as the influence of a diminished partial pressure of oxygen. In many instances these factors seem to have a decided influence, usually retarding, though sometimes stimulating, but they are not either individually or collectively the cause of the sharp termination of the oxygen absorption. H. W. B.

Osmosis in Soils. C. J. LYNDE and J. V. DUPRÉ (*Trans. Roy. Soc. Canada*, 1915, [iii], **9**, 69—80. Compare A., 1915, i, 762).—Further experiments are described the results of which all support the view that the movements of the solutions are due to osmosis.

The final pressure under given conditions is shown to be approximately constant. As regards the duration of the flow, an experiment which was continued for four months showed that the flow at the end of this time was almost as great as at the commencement. The flow increases with increase in temperature and decreases with decrease in the concentration of the soil solution.

N. H. J. M.

Reaction of Soil and Measurements of Hydrogen-ion Concentration. L. J. GILLESPIE (*J. Washington Acad. Sci.*, 1916, **6**, 7—16).—Whilst the lime requirement method of Veitch and all other colorimetric methods are intended to measure the quantity of acid substance present, it is probable that the effects of acidity in soils depend rather on the intensity of the acidity than on the amount of acid. The intensity of acidity and of alkalinity can only be ascertained by measuring the hydrogen-ion concentration.

Electrometric determinations were made with twenty-two soils in an apparatus described with sketches, and colorimetric estimations were made, in which six different indicators were employed. In the latter estimations the soil extracts (5 c.c.) were mixed with the different indicators, and the colours compared with those obtained by adding the same amounts of indicators to 5 c.c. of various regulators of known hydrogen-ion concentration. In every case satisfactory results were obtained with at least one indicator, and in most cases with two.

The hydrogen-ion exponents varied from 4·4 to 8·6, an exponent of seven indicating neutrality, whilst the lower and higher numbers indicate respectively acidity and alkalinity. Four of the soils were sufficiently acid to kill typhoid bacilli in twenty-four hours.

Whilst the two methods gave concordant results, it must be borne in mind that the conditions are not exactly comparable with natural conditions. In drying the soils carbon dioxide is lost, and the solutions employed (2 c.c. of water to 1 gram of soil) are much more dilute than normal soil solutions. N. H. J. M.

The Adsorption of Potassium by the Soil. A. G. McCall, F. M. Hildebrandt, and E. S. Johnston (*J. Physical Chem.*, 1916, **20**, 51—63).—Experiments have been made to determine the adsorption of potassium from a solution of potassium chloride (approximately $1/500N$) by a sandy loam soil and the removal of the adsorbed potassium by leaching with distilled water. Tables are given showing the concentration of the potassium chloride in successive fractional percolates. From the results obtained with the finely pulverised soil it appears that the water is adsorbed more rapidly than the dissolved salt, resulting in an increase in the concentration of the percolates as compared with that of the original solution. This so-called negative absorption is still clearly marked when a correction is applied for the salt which is given up by the soil to the solution during the period of percolation. H. M. D.

Displacement of Potassium and Phosphoric Acid Contained in Certain Rocks by some Substances Used as Fertilisers. G. André (*Compt. rend.*, 1916, **162**, 133—136. Compare A., 1914, i, 127).—Finely-ground glauconite, in quantities of 10 grams, was triturated with water containing 1 gram of one of the following substances: calcium carbonate, sodium chloride, sodium nitrate, ammonium sulphate, calcium sulphate, and the percentage of potassium rendered soluble determined. The results obtained are in the same order as those for microcline felspar (*loc. cit.*), but a higher percentage of the total potassium was rendered soluble. The maximum displacement of potassium was obtained with ammonium sulphate, nearly 10% being rendered soluble.

Similar experiments were performed with a sample of Canadian apatite, the salts used being ammonium carbonate, sodium nitrate, potassium carbonate, and potassium nitrate, the amounts of phosphoric acid rendered soluble being determined. Negative results were obtained with three out of the four salts, potassium carbonate being the only one which extracted any phosphoric acid, and this only to the extent of 0·35% of the total amount present in the apatite. W. G.

Nitrogen, Chlorine, and Sulphates in Rain and Snow. Bonnibal Artis (*Chem. News*, 1916, **113**, 3—5).—Fifty-one samples of rain and snow were examined at Cornell College during the period October, 1914, to June, 1915. The following results, expressed as parts per million, were obtained: Nitrate, 0·005—0·80; nitrite, 0·00025—0·005; nitrogen in free ammonia, 0·03—0·889; nitrogen in albuminoid ammonia, 0·12—1·19; chlorine, 3·5—21·30; sulphate, 1·7—38·0. The chlorine was most constant, being 7·1 parts per million in thirty of the samples. The total fall during the period amounted to 15·35 inches of rain and 37·75 inches of snow. W. P. S.

Organic Chemistry.

Boiling and Condensing Points of Alcohol–Water Mixtures. P. N. EVANS (*J. Ind. Eng. Chem.*, 1916, **8**, 260—262).—The relations existing between the boiling point or condensing point and the composition of the liquid and vapour phases of water–alcohol mixtures are given in tabular and graphic form. A table is also given showing the boiling points corresponding with different alcohol content of alcohol–water mixtures; it is also possible to ascertain from this table the approximate composition of both liquid and vapour (or distillate) at any moment during the distillation of a mixture. W. P. S.

Preparation of Unsaturated Alcohols. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 288271; from *J. Soc. Chem. Ind.*, 1916, **35**, 385).—γ-Methylbutinenol and its homologues are reduced by sodium, zinc dust and acetic acid, copper–zinc dust, colloidal palladium, or nickel to γ-methylbutenol and its homologues, which are convertible into isoprene and its homologues by elimination of water. Details are given of the reduction of γ-methylpentinenol to γ-methylpentenol, and of *cyclo*hexanolacetylene to *cyclo*hexanolethylene. G. F. M.

***iso*Amyl Xanthates.** L. GÓMEZ (*Anal. Fis. Quim.*, 1916, **14**, 91—102).—A summary of the literature of the xanthates, and an account of the conductivity, degree of dissociation, and other ionic properties of potassium *iso*amyl xanthate. A. J. W.

Periodic Evolution of Carbon Monoxide. JOHN STANLEY MORGAN (T., 1916, **109**, 274—283).—The conditions determining the periodic evolution of carbon monoxide by the dehydration of formic acid with concentrated sulphuric acid have been studied. The purest acid did not give periods, and fractions from active acids were found to behave differently, the higher fractions being increasingly active, and inducing periodic evolution when added in small quantities to inactive acids. Orthoformic ester, methyl, ethyl, propyl and amyl alcohols, glycerol, gelatin, and dextrin also induced periodicity. Nitric acid changed the whole nature of the reaction, a blue compound being produced, followed by a violent evolution of gas. From a consideration of all the evidence, the author concludes that the periodic evolution of gas is a supersaturation phenomenon. The paper is illustrated by curves obtained by the use of Ostwald's chemograph. G. F. M.

Acetic Anhydride. J. T. HEWITT and C. H. LUMSDEN (*J. Soc. Chem. Ind.*, 1916, **35**, 210—213).—A review of methods available for the technical preparation of acetic anhydride. The authors consider that the chlorides of sulphur or phosphorus are the most suitable dehydrating agents for the purpose. G. F. M.

The Formation of Pyruvic Acid from Malic Acid by Micro-organisms. M. W. BEYERINCK and T. FOLPMERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1198—1200).—The oxidation of malic acid with the formation of pyruvic acid according to the equation $C_4H_6O_5 + O = C_3H_4O_3 + CO_2 + H_2O$, is brought about by the action of many different species of micro-organisms, which are divided into groups according to their activity. *l*- and *i*-Malic acids are acted on equally readily, but the formation of pyruvic acid takes place much less easily when the *d*-acid is employed in the experiments. H. M. D.

The Non-existence of Metatartaric Acid. J. J. L. ZWIKKER (*Rec. trav. Chim.*, 1916, **35**, 254—259).—The author considers that the substance described in the literature as metatartaric acid is really a mixture of superfused tartaric acid and some substances at present not sufficiently studied.

Tartaric acid was gently heated over the flame until it was all molten, and then kept in an oven at 120—125° in a flask plugged with cotton-wool. After several hours crystals began to separate, and, on gently shaking, the whole mass solidified. The solid mass was shaken with a mixture of dry alcohol and ether (1 : 10), and the remaining solid examined. It was found to be homogeneous and to possess exactly the physical properties of tartaric acid, and its calcium salt was almost insoluble. The author explains Bruhat's results obtained in his polarimetric examination of fused tartaric acid (compare A., 1915, i, 496) on the ground that, during the fusion, very small amounts of anhydrides are formed, which probably have a high rotatory power, but escape detection by volumetric analysis. The difference in solubility of the salts of the so-called metatartaric acid and of tartaric acid itself is probably due to the retarding influence of polymolecular substances, and the slow conversion in water of metatartaric into tartaric acid is only a slow crystallisation of impure tartaric acid. W. G.

Compounds of Iron, Manganese, Lead, and the Metals of Group II. SPENCER UMFREVILLE PICKERING (T., 1916, **109**, 235—250).—The existence has been established of a large number of metallo-compounds of a similar nature to those of copper, nickel, and cobalt (T., 1915, **107**, 942). Thus by various methods, of which a detailed description is given, such as, for example, by the action of an alkali hydroxide on the organic salt of the metal, by dissolving the hydroxide of the metal in the acid in question and precipitating with alcohol, or by mixing solutions of a soluble inorganic salt with the potassium salt of the organic acid, the existence of metallo-compounds of iron, manganese, lead, and the metals of the periodic group II with citric, tartaric, and malic acids has been proved, and in most cases the compounds have been isolated. These compounds are always much more soluble than the normal crystallised salt, and from solutions of the former the normal salt is deposited by more or less rapid isomeric change. The theoretical bearing which the existence of these compounds have on the question of valency is discussed. G. F. M.

Stereochemical Studies. I. Stereochemistry of the Thiolmalic Acids. BROR HOLMBERG (*Arkiv Kem. Min. Geol.*, 1916, **6**, No. 1, 1—22).—Thiolmalic acid is best obtained from xanthosuccinic acid and ammonia by Biilmann's method (A., 1905, i, 625), using, however, aqueous instead of alcoholic ammonia. The author has found that the pure acid is readily obtained by the prolonged action (several days) of potassium hydrogen sulphide on bromosuccinic acid (Carius's method); the more dilute the solution used, the less is the quantity of thiodisuccinic acid formed at the same time. The pure inactive acid has m. p. 149—150°. The *calcium* salt, $C_4H_4O_4SCa,2H_2O$, is crystalline and sparingly soluble in water.

l-*Thiolmalic acid* is obtained from *l*-xanthosuccinic acid by the action of ammonia. It has m. p. 152—153°, and is somewhat less soluble than the inactive acid, which is readily soluble in water and alcohol, fairly so in ether, but very sparingly so in benzene. The following specific rotations, $[\alpha]_D^{17}$, were obtained for solutions containing about 1 gram of the acid in 20 c.c. of the solvent: in ethyl acetate, $-76\cdot5°$; in acetone, $-75\cdot8°$; in absolute alcohol, $-64\cdot8°$; in water, $-46\cdot7°$. The aqueous solution, after half-neutralisation with potassium hydroxide, gave $-41\cdot3°$, and after complete neutralisation $-43\cdot5°$.

d-*Thiolmalic acid* was obtained from *d*-xanthosuccinic acid, and has m. p. 152—153°. The specific rotations in solutions of the above concentration were: in ethyl acetate, $+76\cdot5°$; in acetone, $+76\cdot1°$; in absolute alcohol, $+64\cdot4°$.

A solution of 1·5 grams of *l*-thiolmalic acid in 40 c.c. of *N*-sulphuric acid underwent no appreciable racemisation when heated for six hours on the water-bath. A pure $M/4$-solution was racemised to the extent of 7·1% in the same time, whilst the racemisation in solutions to which $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$-mol. potassium hydroxide per equivalent of acid had been added was respectively 53·6%, 60·2%, and 33·2%. Heating in neutral, weakly alkaline or potassium hydrogen sulphide solution had no effect.

The action of potassium hydrogen sulphide on *l*-bromosuccinic acid under varying conditions of concentration, both absolute and relative, was studied, as also the effect of the presence of potassium sulphate, potassium bromide, and strontium bromide (bromide ion and cation catalysis). According to the conditions, varying mixtures of *d*- and *l*-thiolmalic acids were obtained. The results can be explained by the following reaction scheme, which is similar to that put forward in other cases (compare A., 1913, i, 824; ii, 942; 1914, i, 139, 248):

$$(1)\ l\text{-}CO_2M\cdot CHBr\cdot CH_2\cdot CO_2M + MSH = d\text{-}CO_2M\cdot CH(SH)\cdot CH_2\cdot CO_2M + MBr;$$

$$(2a)\ l\text{-}CO_2M\cdot CHBr\cdot CH_2\cdot CO_2M \rightleftarrows d\text{-}CO_2M\cdot \overline{CH\cdot CH_2\cdot CO_2} + MBr;$$

$$(2b)\ d\text{-}CO_2M\cdot \overline{CH\cdot CH_2\cdot CO_2} + MSH = l\text{-}CO_2M\cdot CH(SH)\cdot CH_2\cdot CO_2M.$$

In agreement with this it was found that *l*-thiolmalic acid could be obtained by the action of potassium hydrogen sulphide on the *d*-malic lactonic acid corresponding with *l*-bromosuccinic acid.

By the oxidation of the active thiolmalic acids with air or with ferric chloride, the corresponding l- and d-*dithiodisuccinic acids*, $S_2(C_4H_5O_4)_2$, m. p. 167—168°, were obtained. The solutions of 0·5 gram in 10 c.c. of various solvents gave the following specific rotations, $[\alpha]_D^{17}$: in absolute alcohol, −272·9° and +272·8°; in acetone, −269·3° and +270·2°; in water, −290·5°. The d-*barium dithiodisuccinate*, $S_2(C_4H_3O_4Ba)_2,4H_2O$, is less soluble in hot than in cold water.

r-*Dithiodisuccinic acid*, m. p. 172—173°, was obtained by mixing in acetone solution equal quantities of the *l*- and *d*-isomerides. When inactive thiolmalic acid is oxidised, a mixture of the racemic and meso-acids is obtained which is difficult to separate.

T. S. P.

Resolution of Racemic Sugars by Means of Optically Active Amyl Mercaptans. Certain Mercaptals. E. Votoček and V. Veselý (*Zeitsch. Zuckerind. Böhm.*, 1916, **40**, 207—211).—Optically active amyl mercaptan is a suitable substance for resolving racemic aldoses. l-*Arabinose*-d-*amyl mercaptal* crystallises from dilute alcohol in long, flat needles, m. p. 114—116°. d-*Arabinose*-d-*amyl mercaptal* crystallises in thin, hexagonal plates, m. p. 118—120°; it is less soluble than the *l*-form. When *i*-arabinose is resolved, the *d*-mercaptal is obtained in a pure condition after five crystallisations, and the *l*-mercaptal may be recovered from the mother liquors. The *d*-amyl mercaptals of rhodeose and fucose have approximately the same melting point and solubility, the latter being very slight; they may be distinguished from each other by the different form of their crystals as seen under the microscope.

W. P. S.

Plant Colloids. VI. The Alkali Starches. Max Samec (*Koll. Chem. Beihefte*, 1916, **8**, 33—62. Compare A., 1915, i, 941).—The changes occurring in starch when its solutions are acted on by alkalis, have been submitted to examination by a study of the changes in the physical properties of the solutions. From a comparison of the behaviour of ordinary and phosphorus-free starches, it would seem that the initial changes produced by alkalis are due to the action of the alkali on the phosphoric acid group of the starch molecule. Further action results in the combination of the alkali with other groups in the starch molecule and in the peptonisation of the starch.

H. M. D.

The Acetylation and Acetolysis of Cellulose and Starch by Means of Acetic Anhydride. J. Böeseken, J. C. van den Berg, and A. H. Kerstjens (*Rec. trav. chim.*, 1916, **35**, 320—345).—A study of the acetylation of cellulose and starch in the presence of certain catalysts. A difference is noticeable between the acetylation of cellulose and starch, caused probably by the different character

of their surfaces, but the order of action of the different catalysts tried is almost the same for cellulose as for starch.

The cellulose used was Swedish filter-paper, the catalysts tried being sulphuric, hydrobromic, and hydriodic acids and acetyl iodide, all of which gave positive results; and pyridine, ethylamine, sodium acetate, acetyl chloride, hydrochloric acid, and a number of inorganic salts, all of which gave negative results. Hydriodic acid and acetyl iodide were more satisfactory than hydrobromic acid, and this in turn than hydrochloric acid, but the best catalyst was without doubt sulphuric acid. The reaction is probably a series of acetylations and hydrolyses, the latter being indicated, if the action is prolonged, by a continuous rise in the acetyl value of the product.

The velocity of acetylation of starch is less than that of cellulose. The best catalyst for starch is hydriodic acid. In the case of sulphuric acid an increase in the amount of acid used produces an acceleration of the acetylation, but not to an extent proportional to the amount of the catalyst used. W. G.

Preparation of Diethylamine on a Large Scale in the Laboratory. T. SLATER PRICE, S. A. BRAZIER, and A. S. WOOD (*J. Soc. Chem. Ind.*, 1916, **35**, 147—149).—The usual method, consisting in the formation and hydrolysis of *p*-nitrosodiethylaniline, was adopted, with certain modifications in working. In preparing the nitroso-compound the temperature was maintained at 5—8° during the addition of the nitrite solution by adding ice to the reaction mixture. The hydrolysis was carried out in a 10-gallon iron drum, and the diethylamine was condensed directly instead of being absorbed in hydrochloric acid, a guard-tube containing rods moistened with acid being sufficient to avoid loss through incomplete condensation of the base. Distillation over sodium hydroxide of the concentrated aqueous amine which collected in the receiver gave a pure diethylamine boiling constantly at 56°, in 86·5% yield, calculated on the diethylaniline originally taken. The presence of 5—10% of monoethylaniline in the starting material does not adversely affect the purity of the product. A permanent apparatus, comprising certain labour-saving devices for the carrying out of the above operations is described in detail. G. F. M.

Decompositions of Sodium Diacetamide and Potassium Acetamide. JITENDRA NATH RAKSHIT (T., 1916, **109**, 180—184).—When sodium diacetamide is decomposed by heat, a mixture of acetonitrile and acetone distils off, and a residue of sodium carbonate quite free from cyanide remains, the chemical change being represented by the equation: $2C_4H_6O_2NNa = Na_2CO_3 + 2MeCN + COMe_2$; this result favours the view that the constitution of sodium diacetamide, at least under the conditions of the decomposition, is $NAc{:}CMe{\cdot}ONa$. With potassium acetamide the products of decomposition are potassium hydroxide and acetonitrile, together with smaller quantities of potassium cyanide, ammonia, a gas, and an insoluble oil.

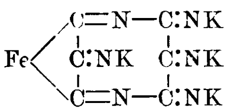
In an endeavour to prepare sodium acetamide by the interaction of sodium ethoxide and acetamide in alcoholic solution, it was found that the acetamide underwent hydrolysis into ammonia and acetic acid, the necessary water being produced by the dehydration of some of the alcohol to ether in the presence of sodium ethoxide (compare Scott, T., 1909, **95**, 1200; Rây and Rakshit, T., 1912, **101**, 217). When an aqueous-alcoholic silver nitrate solution is added gradually to an alcoholic solution of sodium diacetamide, a pale orange precipitate is obtained, which disappears on shaking, being soluble in the presence of excess of sodium diacetamide; with a larger proportion of silver nitrate a permanent, brown precipitate is obtained which turns black in a few minutes.

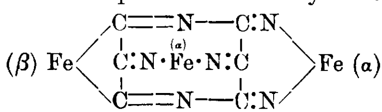
The decomposition of sodium diacetamide by a little water at the ordinary temperature appeared to occur slowly, ammonia being gradually evolved, whilst the residual solid matter weighed 7·75% more than the original substance. Analysis of the residue showed this to consist of sodium acetate and diacetamide, the total change being representable by the equation: $2NAc_2Na + 2H_2O = 2AcONa + NHAc_2 + NH_3$. D. F. T.

Preparation of Acidyl-α-bromo-α-ethylbutyrylcarbamides. Farbenfabriken vorm. F. Bayer & Co. (D.R.-P. 286760; from *J. Soc. Chem. Ind.*, 1916, **35**, 197).—Acidylbromoethylbutyrylcarbamides of the general formula $NHR\cdot CO\cdot NH\cdot CO\cdot CBrEt_2$ are obtained by the action of acid amides on α-bromo-α-ethylbutyrylcarbamic acid haloids or α-bromo-α-ethylbutyrylcarbimide, or of α-bromo-α-ethylbutyramide on acidylcarbimides or acidylcarbamic acid haloids. They are sparingly soluble substances, and possess sedative and soporific properties. G. F. M.

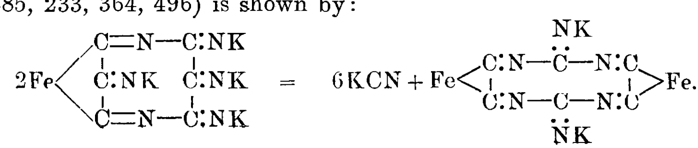
New Constitutional Formulæ for Ferrocyano-compounds. G. Denigès (*Bull. Soc. chim.*, 1916, [iv], **19**, 79—90).—A theoretical paper, in which the author proposes new constitutional formulæ for ferro-, ferri- and perferri-cyanides, and on the basis of these formulæ explains the reactions which these compounds are known to undergo.

Potassium ferrocyanide is given the constitution represented by formula I, the corresponding ferrous ferrocyanide being represented by formula II. The decomposition of potassium ferrocyanide at


(I.)

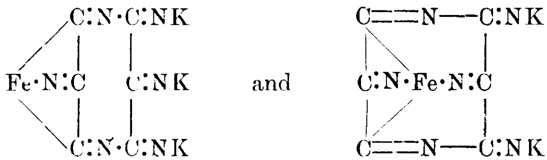

(II.)

red heat giving Williamson's salt (compare Étard and Bémont, A., 1885, 233, 364, 496) is shown by:

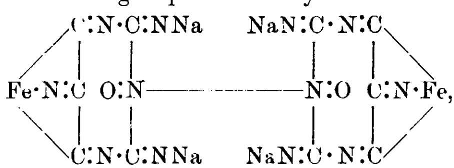


The decomposition of this salt on further heating and the behaviour of ammonium ferrocyanide and hydroferrocyanic acid on heating are similarly explained. The constitutions of the additive compounds formed by the alkali ferrocyanides, such as Bunsen's salt, $(NH_4)_4Fe(CN)_6,2NH_4Cl$, the compounds, $K(NH_4)_3Fe(CN)_6,2NH_4Cl$ and $KH_2(NH_4)Fe(CN)_6,2NH_4Cl$, and the ethereal compound, $H_4Fe(CN)_6,2Et_2O$, described by Étard and Bémont (*loc. cit.*), and the compound $H_4Fe(CN)_6,6EtOH,2HCl$, prepared by Buff, are all readily explained on the basis of the above formula for ferrocyanides.

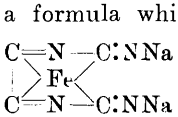
The formulæ given for potassium ferricyanide and potassium perferricyanide are respectively:



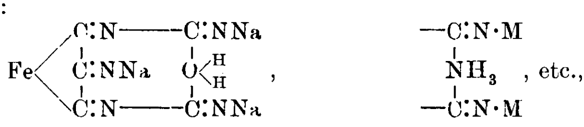
the nitroprussides being represented by:



a formula which explains the decomposition of these compounds



when heated in a vacuum, giving nitrous oxide, cyanogen, and two molecules of a tetracyanide analogous to the platinocyanides (annexed formula). Finally, Hofmann's salts, such as sodium ferropentacyanide, $Na_3[Fe(CN)_5,H_2O]$, and its derivatives, where the H_2O is replaced by different molecules, for example, NH_3, $M\cdot CN$, $NO_2\cdot M$, SO_3M_2, AsO_2M, may be represented by the formulæ:



and in the case of the carboxylferrocyanides, the median group $\overset{|}{\underset{|}{C}}\!:\!N\cdot M$ is replaced by the group $\overset{|}{\underset{|}{C}}\!:\!O$. W. G.

Chloro- and Bromo-triethylphosphinoacetaldehydes. WILLIAM CALDWELL (T., 1916, **109**, 283—287).—The results of an endeavour to prepare the phosphorus compound analogous to the aldehyde compound intermediate between choline and betaine (compare Hofmann, *Proc. Roy. Soc.*, 1860, **10**, 614).

Triethylphosphine and monochloroacetal in a sealed tube react with formation of *chlorotriethylphosphinoacetal* as a viscous liquid

substance (*platinichloride*, $[C_{12}H_{28}O_2Cl]_2PtCl_4$, long, yellow needles; *aurichloride*, an oil). This substance, when heated with hydrochloric acid at 100° in an open dish, yielded *chlorotriethylphosphinoacetaldehyde*, $C_8H_{18}OClP$, stellate masses of leaflets (*platinichloride*, minute, orange-yellow octahedra), which reduces ammoniacal silver nitrate, and when added with a fragment of sodium amalgam to diazobenzenesulphonic acid in water gives a reddish-violet coloration.

Monobromoacetal and triethylphosphine interact at the ordinary temperature, yielding a colourless liquid, presumably *bromotriethylphosphinoacetal*.

When heated together in a sealed tube for eight hours at 100°, bromoacetaldehyde and triethylphosphine react, producing *bromotriethylphosphinoacetaldehyde*, $C_8H_{18}OBrP$, deliquescent needles. These phosphorus compounds are characterised by a marked unpleasant odour. D. F. T.

Equilibrium Relations among Aromatic Hydrocarbons Produced by Cracking Petroleum. W. F. RITTMAN and T. J. TWOMEY (*J. Ind. Eng. Chem.*, 1916, **8**, 20—22. Compare this vol., i, 1, 133).—Definite relations exist between the quantities of various aromatic hydrocarbons formed when petroleum is cracked, the percentages being fixed by the degree of cracking. The factors which control the latter may be represented by the specific gravity of the cracked oil. Toluene and xylene show the same variation in percentage formation, xylene being present in about one-half the quantity of the toluene; both are at a maximum (10·8% xylene and 17·8% toluene) in a recovered oil of D 0·95. Benzene formation requires more vigorous cracking than is needed for the production of toluene and xylene; the maximum yield is at a point where the quantities of toluene and xylene have decreased considerably. Naphthalene begins to form at a point where the toluene–xylene content passes its maximum, indicating that naphthalene is a product of the decomposition of the monocyclic hydrocarbons; the same applies to the formation of anthracene. Benzene, toluene, and xylenes may be estimated in a cracked oil as follows: The oil is distilled and the first fraction (up to 175°) is twice fractionally distilled, being divided into the benzene fraction, b. p. up to 95°, the toluene fraction, b. p. 95—120°, and the xylene fraction, b. p. 120—175°. Knowing the specific gravities of the pure hydrocarbons and determining those of the distillates, the quantities of the three hydrocarbons are found by a simple calculation.

W. P. S.

Action of Ozone on Organic Compounds. IV. C. HARRIES (*Annalen*, 1916, **411**, 158—160. Compare A., 1915, i, 966).—An acknowledgment that Wallach had already isolated *cyclo*pentyl*cyclo*pentene and allied compounds (A., 1912, i, 568), and a reference to the decomposition of hexamethylpentamethylenediammonium hydroxide effected by von Braun (*ibid.*, 165). J. C. W.

Preparation of Dichloroanthracene Hexachloride and Dichloroanthracene Octachloride. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 289133; from *J. Soc. Chem. Ind.*, 1916, **35**, 353).—Sulphuryl chloride is used instead of carbon tetrachloride as prescribed in the chief patent (D.R.-P. 284790). Thus by chlorinating a solution of 9:10-dichloroanthracene in sulphuryl chloride in presence of a trace of iodine, the octachloride is precipitated, and the hexachloride formed in solution. G. F. M.

Preparation of Metallic Derivatives of Organic Nitrogenous Compounds. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 287601; from *J. Soc. Chem. Ind.*, 1916, **35**, 170).—Organic compounds containing hydrogen united with nitrogen, when heated with metallic magnesium or aluminium or mixtures of the two, if necessary, in presence of high boiling, indifferent organic solvents and of catalysts, are converted into metallic derivatives, which are useful in condensation reactions, for example, with halogen and sulphur compounds, alcohols, aldehydes, ketones, acids, nitro- and nitroso-compounds. Aluminium anilide may be prepared by heating aluminium shavings (5 parts) with aniline (100 parts) at 150—160°, the temperature being gradually raised to the boiling point, until the product solidifies on cooling. G. F. M.

Process for the Introduction of Amino-groups into Aromatic Compounds. J. F. DÉ TURSKI (D.R.-P. 287756; from *J. Soc. Chem. Ind.*, 1916, **35**, 170).—Aromatic compounds which dissolve in, but are not readily sulphonated by, sulphuric acid are converted on treatment with sulphuric acid and hydroxylamine, if necessary with the addition of metallic compounds, into their amino-derivatives. Such are anthraquinone, benzophenone, indanthrene, xanthone, quinoline, and pyridine. Aromatic substances, such as benzene, naphthalene, and anthracene, which do not dissolve in concentrated sulphuric acid or are easily sulphonated, are converted first into sulphonic acids and then by the further action of the hydroxylamine and sulphuric acid into amino-derivatives.
G. F. M.

Preparation of a [Zinc] Salt of Phenylbenzyldimethylammoniumdisulphonic Acid. CHEM. FABRIK ROHNER & CO. (Eng. Pat., 1914, 24695; from *J. Soc. Chem. Ind.*, 1916, **35**, 248).—Phenylbenzyldimethylammonium zinc chloride (Swiss Pat. 64016) is converted into a disulphonic acid by treatment at 70—80° first with sulphuric acid monohydrate, and then, after expulsion of the hydrogen chloride by means of air, with 70% fuming sulphuric acid. The excess of sulphuric acid is removed by barium or calcium carbonate, and the neutral solution on evaporation yields the zinc salt as a yellow, hygroscopic powder. G. F. M.

Preparation of Benzoic and Sulphobenzoic Acids. A. HEINEMANN (Eng. Pat., 1914, 23575; from *J. Soc. Chem. Ind.*, 1916, **35**, 170).—Toluene in presence of concentrated sulphuric acid, or

a concentrated aqueous solution of toluene-*o*- or *p*-sulphonic acid, is treated with ozonised oxygen at a temperature just below the boiling point of toluene or just below 100° respectively, whereby the methyl group is oxidised to carboxyl. G. F. M.

Preparation of Boro-disalicylic Acid. A. FOELSING (D.R.-P. 288338; from *J. Soc. Chem. Ind.*, 1916, **35**, 385).—Free *boro-disalicylic acid*, $HO{\cdot}B(O{\cdot}C_6H_4{\cdot}CO_2H)_2$, is prepared by precipitating the insoluble sulphide from an aqueous solution of one of its salts with a suitable metal. It is easily soluble in water, alcohol, acetone, and glycerol, has a bitter taste, is non-poisonous, and is more strongly bactericidal than mixtures of boric and salicylic acids or their salts. It is useful as an internal antiseptic. G. F. M.

Preparation of Arylamides of 2:3-Hydroxynaphthoic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 289027; from *J. Soc. Chem. Ind.*, 1916, **35**, 353).—Arylamides of 2:3-hydroxynaphthoic acid are obtained by heating the acid with the arylamide of a volatile organic acid. Thus, using acetanilide, the anilide of hydroxynaphthoic acid is produced. G. F. M.

The Ferric Salts of Unsubstituted Mono- and Poly-basic Organic Acids. R. F. WEINLAND and FR. PASCHEN (*Zeitsch. anorg. Chem.*, 1915, **92**, 81—118).—The ferric salts of the unsubstituted monocarboxylic acids hitherto studied, with one exception, are salts of complex bases, composed of three iron atoms and six or less acid residues. On the other hand, the lower dicarboxylic acids form complex anions containing iron. Ferric formate contains both a complex anion and a triferric cation (Weinland and Reihlen, A., 1913, i, 1300). Glycollic and tartaric acids form complex anions; *m*- and *p*-hydroxybenzoic acids form triferrihexa-acid bases, whilst salicylic acid forms both. Higher unsubstituted acids have now been examined.

α-Naphthoic acid forms an insoluble, orange ferric salt with the ratio 3Fe:7 acid. This is *hexanaphthoatotriferric naphthoate*. The *nitrate* forms dark red crystals containing $2H_2O$, and the *perchlorate* anhydrous crystals. Cinnamic acid forms a very insoluble yellow salt with the ratio 6Fe:13 acid. It is proved to contain a hexacinnamotriferric base by yielding a mixed *nitrate–cinnamate* and a *perchlorate–cinnamate*. The precipitate of *ferric pyromucate* is quite similar in composition to the cinnamate, and the *perchlorate–pyromucate* is also similar, but a pure *chloride* of the hexapyromucotriferric base is obtained with $3H_2O$ as long, yellow needles.

2-Phenylquinoline-4-carboxylic acid gives a nearly white precipitate with the ratio 3Fe:7 acid. This is quite similar in constitution to the acetate, benzoate, and naphthoate. A *chloride* with the ratio 3Fe:4Cl is also obtained.

Ferric laurate is of similar constitution, and is probably $Fe_3(C_{12}H_{23}O_2)_6(OH)_3$. It is soluble in chloroform and benzene.

The phthalic acids behave in similar manner, 3 mols. of phthalic

acid replacing 6 mols. of monocarboxylic acid in the cation. The *nitrate* contains two of these cations, two NO_3 groups, and one phthalic residue; the *perchlorate* three complex cations, two ClO_4 groups, and one phthalic residue.

The camphoric acid precipitate has the ratio 3Fe:7 acid, and forms a *perchlorate*, 6Fe:9 camphoric acid:$2ClO_4$, and a *nitrate*, 9Fe:13 camphoric acid:$3NO_3$.

Succinic acid, unlike oxalic and malonic acids, forms a ferric salt with complex cation, the *nitrate–succinate* containing 6Fe:7 succinic acid:$2NO_3$. The corresponding salt from fumaric acid is exactly similar. *Ferric fumarate* resembles the phthalate, whilst maleic acid does not yield a crystalline salt. A definite ferric oxalate has not been obtained.

Hemimellitic acid yields a ferric salt with the ratio 3Fe:2 acid, probably also a triferric derivative, and the salt of aconitic acid is similar.

It is necessary to take the subsidiary valencies into account in formulating the salts with complex cations. C. H. D.

Preparation of Aromatic Aldehydes. J. LONGMAN (Eng. Pat., 1915, 3152; from *J. Soc. Chem. Ind.*, 1916, **35**, 384).—Aromatic aldehydes are produced by the action of carbon monoxide on the corresponding hydrocarbons under pressure in presence of aluminium chloride with or without the addition of a little hydrochloric acid. Halogenised hydrocarbons react in a similar way. Details are given of the preparation of benzaldehyde, *p*-tolualdehyde, and *p*-chlorobenzaldehyde. The pressures employed varied from 50 to 90 atmospheres. G. F. M.

Dehydrodivanillin. K. ELBS and H. LERCH (*J. pr. Chem.*, 1916, [ii], **93**, 1—9).—It is already known that the action of persulphates can effect the oxidation of salicylaldehyde to gentisaldehyde by the conversion of a hydrogen atom into a hydroxyl group (Neubauer and Flatow, A., 1907, i, 771). It is now found that anisaldehyde undergoes almost quantitative conversion into anisic acid when warmed with an aqueous solution of sodium persulphate, but that vanillin and piperonal undergo oxidation with formation of a diphenyl nucleus.

The result obtained in the oxidation of vanillin with a persulphate depends largely on the metal with which the persulphate radicle is combined; thus, whereas the sodium salt gives an almost quantitative conversion into dehydrodivanillin, the potassium and ammonium salts yield only 60—70% and 50% respectively. The dehydrodivanillin obtained by Tiemann (A., 1886, 238) by oxidation of vanillin with ferric chloride was very pure, although the yield was only moderate; the product obtained with sodium persulphate is contaminated by a slight amount of a persistent impurity. By effecting the oxidation with sodium persulphate in the presence of a little ferrous sulphate, the advantages of purity and good yield are obtained together; the crude product is then

further purified by dissolving in a solution of barium hydroxide or sodium hydroxide and reprecipitating with hydrochloric acid.

Dehydrodivanillin dimethyl ether, obtained by the action of methyl sulphate on dehydrodivanillin in warm alkaline solution, gives a *diphenylhydrazone*, $[\cdot C_6H_2(OMe)_2\cdot CH:N\cdot NHPh]_2$, yellow needles, m. p. 234°. Boiling with acetic anhydride converts dehydrodivanillin into the *diacetyl* derivative,

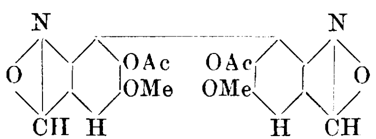
$$C_{12}H_4(OAc)_2(OMe)_2(CHO)_2,$$

colourless needles, m. p. 117° (*phenylhydrazone* difficult to purify on account of its easy solubility in alcohol), which is oxidised by potassium permanganate in acetone solution to *diacetyldehydrodivanillic acid*, $C_{12}H_4(OAc)_2(OMe)_2(CO_2H)_2$, colourless needles, m. p. 140°; this, on hydrolysis with sodium hydroxide solution, gives *dehydrodivanillic acid*, $C_{12}H_4(OH)_2(OMe)_2(CO_2H)_2$, colourless needles, m. p. 295°; the *sodium*, *potassium*, *calcium*, and *barium* salts were obtained as gelatinous precipitates very easily soluble in water. In the oxidation of diacetyldehydrodivanillin, the resulting diacetyldehydrodivanillic acid is accompanied by *diacetonylidenediacetyldehydrodivanillin* [2 : 2′-*diacetoxy*-3 : 3′-*dimethoxy*-5 : 5′-*di*(γ-*keto*-Δ^α-*butenyl*)-*diphenyl*], $C_{12}H_4(OAc)_2(OMe)_2(CH:CHAc)_2$, small, colourless crystals, m. p. 246° (*dibromophenylhydrazone*, yellow crystals, m. p. 226—227°), which becomes the chief product if an excess of potassium permanganate is avoided.

When treated with a mixture of sulphuric and fuming nitric acids at −10°, dehydrodivanillin dimethyl ether is converted into *dinitrodehydrodivanillin dimethyl ether*,

$$C_{12}H_2(NO_2)_2(OMe)_4(CHO)_2,$$

colourless needles, m. p. 242°, decomp. near 245°. In a similar manner, diacetyldehydrodivanillin can be nitrated to *dinitrodiacetyldehydrodivanillin*, $C_{12}H_2(NO_2)_2(OAc)_2(OMe)_2(CHO)_2$, colourless needles, m. p. 90° (decomp.). Reduction of this compound in acetic acid solution with tin gives rise to *diacetyldimethoxydehydrodianthranil* (annexed formula), colourless leaflets, m. p. 211°. The formation of this compound is of importance as allowing the nitro-group in dinitrodiacetyldehydrodivanillin and also probably in the dinitrodehydrodivanillin dimethyl ether, to be definitely assigned to the ortho-position to the aldehyde group, whilst it also serves to indicate the position of the diphenyl linking.



The nitration of diacetyldehydrodivanillic acid with a cooled mixture of sulphuric and fuming nitric acids yields *dinitrodiacetyldehydrodivanillic acid*, $C_{12}H_2(NO_2)_2(OAc)_2(OMe)_2(CO_2H)_2$, colourless needles, m. p. 270° (decomp.). D. F. T.

Preparation of *N*-substituted 4 : 4′-Diaminodiarylthioketones and their Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 287994; from *J. Soc. Chem. Ind.*, 1916, **35**, 352—353).—Thioketones are obtained by heating *N*-substituted 4 : 4′-diaminodiarylmethanes, such as 4 : 4′-tetramethyldiaminodiphenylmethane,

with polysulphides in a reflux apparatus until the methane base has disappeared. Excess of polysulphides and sulphur are removed by boiling the product with dilute sodium sulphide solution, and any unchanged methane base in the residue is extracted by means of alcohol or dilute hydrochloric acid. The yield of 4 : 4′-*tetramethyl-diaminothiobenzophenone* thus obtained is good, and in a similar way the *tetraethyl* derivative, and s-4 : 4′-*dimethylamino*-3 : 3′-*di-aminothiobenzophenone* may be prepared from their corresponding methane bases. G. F. M.

Preparation of 4 : 4′-Diaminodiarylketones and their Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 289108; from *J. Soc. Chem. Ind.*, 1916, **35**, 353).—Instead of using *N*-substituted 4 : 4′-diaminodiarylmethanes or their derivatives as prescribed in the chief patent (preceding abstract), the methane bases themselves or derivatives obtained by substitution in the aryl residue are heated with polysulphides. G. F. M.

Synthesis of Indandiones. V. Constitution of Mellophanic and Prehnitic Acids. MARTIN FREUND and KARL FLEISCHER [with MAX PRAETORIUS] (*Annalen*, 1916, **441**, 14—38. Compare A., 1915, i, 971, and earlier).—The authors have applied their method of synthesising aromatic polycarboxylic acids from indandiones to the synthesis of mellophanic and prehnitic acids, and they show thereby that these acids are the benzene-1 : 2 : 3 : 4- and -1 : 2 : 3 : 5-tetracarboxylic acids, as Baeyer originally supposed and Bamford and Simonsen (T., 1910, **97**, 1908) also demonstrated.

The starting point in these syntheses was the condensation of diethylmalonyl chloride with *p*-xylene for mellophanic acid and with *m*-xylene for prehnitic acid.

Diethylmalonyl chloride and *p*-xylene were made to react in carbon disulphide under the influence of aluminium chloride and 4 : 7-*dimethyl*-2 : 2-*diethylindan*-1 : 3-*dione*, $C_6H_2Me_2{<}{\scriptstyle CO \atop CO}{>}CEt_2$, was isolated in hexagonal leaflets, m. p. 51—52°, b. p. 164—165°/14 mm. This was boiled with 50% potassium hydroxide until a solid separated which was the potassium salt of 6-*diethylacetyl*-2 : 5-*dimethylbenzoic acid* [6-α-*ethylbutyryl*-2 : 5-*dimethylbenzoic acid*], $CHEt_2\cdot CO\cdot C_6H_2Me_2\cdot CO_2H$. The acid crystallised in quadratic leaflets, m. p. 150°, provoked to sneezing, and yielded no phenylhydrazone or esters, as might be expected. On warming with nitric acid (D 1·4), the acid was oxidised to the anhydride of 3 : 6-dimethylbenzene-1 : 2-dicarboxylic acid (Gucci and Grassi-Cristaldi, A., 1892, 872, gave m. p. 96° for the acid; it is now found to be 145·5°). Either the original indandione, or the intermediate acid, or the last-named acid yielded mellophanic acid on heating with fuming nitric acid in a sealed tube at 140° for seven or eight hours. The preparation from the indandione directly was also accompanied by the formation of an intermediate acid, 2 : 2-*diethylindan*-1 : 3-*dione*-4 : 7-*dicarboxylic acid*, $C_6H_2(CO_2H)_2{<}{\scriptstyle CO \atop CO}{>}CEt_2$, prismatic

columns, m. p. 208—211°. This crystallises from hot water, whereas mellophanic acid must be thrown out by adding concentrated nitric acid. Mellophanic dianhydride was also prepared.

The original indandione was reduced to the corresponding hydrocarbon by Clemmensen's method. 4 : 7-*Dimethyl*-2 : 2-*diethylhydrindene*, $C_6H_2Me_2<^{CH_2}_{CH_2}>CEt_2$, was obtained as an oil with a petroleum-like odour, b. p. 140—141°/13 mm., D 0·923, *n* 1·51592.

The condensation of diethylmalonyl chloride with *m*-xylene resulted in the formation of 4 : 6-*dimethyl*-2 : 2-*diethylindan*-1 : 3-*dione* as an aromatic oil, b. p. 168—171°/12 mm., D 1·055. This was hydrolysed to 2-*diethylacetyl*-3 : 5-*dimethylbenzoic acid* [2-α-*ethylbutyryl*-3 : 5-*dimethylbenzoic acid*], which crystallised in hexagonal, flat prisms, m. p. 126—127°, and caused coughing and sneezing. It formed no phenylhydrazone, but yielded a *methyl ester*, $C_{16}H_{22}O_3$, m. p. 69—71°, and it was oxidised by warming with moderately concentrated nitric acid, both in a sealed tube and in an open vessel, to 3 : 5-dimethylbenzene-1 : 2-dicarboxylic acid. The properties of the anhydride and the acid agreed with the description by Noyes (A., 1899, i, 284); the m. p. of the acid was found to be 181°. On further oxidation by means of fuming nitric acid at 140—150°, the anhydride, and also the original indandione, yielded prehnitic acid.

On applying Clemmensen's method to the reduction of the indandione, the expected 4 : 6-*dimethyl*-2 : 2-*diethylhydrindene*, $C_{15}H_{22}$, was only obtained once, as a petroleum-like oil, b. p. 260—270°. In other experiments it appeared that the reduction proceeded to the rupture of the 5-ring, resulting eventually in the production of an *oil*, b. p. 260—270°, which agreed with the formula $C_{15}H_{24}$. J. C. W.

Preparation of β-Aminoanthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 288996; from *J. Soc. Chem. Ind.*, 1916, **35**, 353).—β-Aminoanthraquinones are obtained when μ-halogenoanthracene-β-sulphonic acids or their salts are treated with ammonia in presence of oxidising agents. G. F. M.

Preparation of β-Arylaminoanthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 288464; from *J. Soc. Chem. Ind.*, 1916, **35**, 355).—β-Arylaminoanthraquinones are formed when anthraquinone-2-sulphonic acid or its derivatives or substitution products are heated with aromatic amines and alkali hydroxides or alkyloxides with or without the addition of oxidising agents. On sulphonation they yield valuable wool dyes. Details of the preparation of 2-*anilinoanthraquinone* are given.

G. F. M.

Preparation of Quinizarinsulphonic Acid. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P. 287867; from *J. Soc. Chem. Ind.*, 1916, **35**, 355).—Quinizarin may be sulphonated by heating it with sulphites, the reaction being accelerated by the addition of suitable oxidising agents, such as manganese dioxide, lead peroxide, or sodium hypochlorite. G. F. M.

Preparation of Hydroxyanthraquinonesulphonic Acids. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 288474; from *J. Soc. Chem. Ind.*, 1916, **35**, 355).—1:4-Dihydroxyanthraquinones may be sulphonated by heating with sulphites in the same manner as quinizarin (see preceding abstract). Purpurin gives in this way the 3-sulphonic acid, whereas alizarin-Bordeaux, 1:4:5-trihydroxyanthraquinone, and other dihydroxyanthraquinone derivatives give sulphonic acids differing in constitution from those obtained by the usual sulphonation process. These products seem to be similar in constitution to quinizarin-2-sulphonic acid. G. F. M.

Preparation of Sulphonic Acids of the Anthraquinone Series. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 289112; from *J. Soc. Chem. Ind.*, 1916, **35**, 355).—*p*-Aminohydroxyanthraquinones, *p*-diaminoanthraquinones, and their derivatives may likewise be converted into new sulphonic acids by treatment with sulphites as for quinizarinsulphonic acid in the chief patent (D.R.-P. 287867; see preceding abstracts). G. F. M.

Catalytic Reduction with Platinum. Rôle of the Solvent. J. BÖESEKEN and (MLLE.) P. J. BILHEIMER (*Rec. trav. chim.*, 1916, **35**, 288—298).—A comparison of the hydrogenation of pinene in the presence of finely divided platinum, in different solvents. In every case the same weight of platinum and pinene and the same volume of solvent were used. The solvents used were saturated fatty acids, free from water, ether, absolute alcohol, ethyl acetate, and acetic acid in varying stages of dilution. In nearly every case the absorption of hydrogen was very regular. In formic acid and absolute alcohol, however, the absorption was very slow, and the catalyst was poisoned. In ether the velocity of absorption was low, but the activity of the platinum was only very slightly diminished. Dilution of acetic acid with water also diminished the velocity of absorption in that solvent, but did not poison the catalyst. In ethyl acetate the reduction commenced regularly, but after a time the velocity diminished and became almost zero, the catalyst not being poisoned. Acetic, propionic, butyric, *iso*butyric, and *iso*valeric acids, provided they are perfectly pure, are satisfactory solvents, and all behave in a similar manner. W. G.

Preparation of Norcamphor and its Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 287796; from *J. Soc. Chem. Ind.*, 1916, **35**, 198).—Norcamphor, $C_9H_{14}O$, is obtained from the aqueous distillate when ketopinic acid is heated with diluted sulphuric acid or with phosphoric acid (D 1·72) with simultaneous admission of superheated steam, so that the temperature of the boiling liquid is 137—140° or 165—175° respectively. It boils at 105°/13 mm., and serves as a substitute for camphor. G. F. M.

Carvone. ARNO MÜLLER (*J. pr. Chem.*, 1916, [ii], **93**, 10—24).—When carvone is heated with hydrochloric acid (D 1·19) at 120—125°, isomerisation occurs with formation of carvacrol. The

author favours the view that this change involves the intermediate production of 8-chloro-Δ^6-menthen-2-one (compare Kondakov and Lutschinin, A., 1900, i, 104), which by subsequent intramolecular change and elimination of hydrogen chloride passes into carvacrol; indeed, it is already known that carvone reacts with hydrogen chloride in the cold, giving 8-chloro-Δ^6-menthen-2-one, and this substance, when heated, yields carvacrol almost quantitatively. The *phenylhydrazone* and *semicarbazone* of 8-chloro-Δ^6-menthen-2-one form colourless leaflets, m. p. 134—135°, and colourless needles, m. p. 157—158°/750 mm. (decomp.) respectively.

Dihydrocarvone, when heated with hydrochloric acid (D 1·19) at 120—130°, is rather more resistant than carvone, and gives a somewhat poorer yield of carvenone. The mechanism of the change is probably analogous to that in the preceding case, involving 8-chloromenthan-2-one as an intermediate product which yields carvenone by rearrangement and elimination of hydrogen chloride. 8-Chloromenthan-2-one was prepared by the action of hydrogen chloride on cooled dihydrocarvone, and the properties of the product were found to agree with the description of Kondakov and Gorbunov (A., 1898, i, 145) with the exception of the optical rotation; it is possible, indeed, that the pure substance would be optically inactive; the *phenylhydrazone* and *semicarbazone* of the chloro-compound formed colourless scales, m. p. 39—43°, unstable in the air, and colourless needles, m. p. 142—143°, respectively. 8-Chloromenthan-2-one gives a relatively small yield of carvenone when heated, and for the preparation of this substance the direct treatment of dihydrocarvone with hydrochloric acid is to be preferred.

D. F. T.

Oils of the Coniferæ. V. The Leaf and Twig, and Bark Oils of Incense Cedar. A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1916, **8**, 22—24. Compare A., 1915, i, 83).—The physical and chemical constants of the oils obtained from the incense cedar (*Libocedrus decurrens*), a tree largely restricted in its range to California, were found to be as follows: Leaf (needles) and twig oil, yield, 0·17% to 0·30%; D 0·8655 to 0·8766; n_D^{15} 1·4754 to 1·4778; α_D^{20} $-3·20°$ to $+38·68°$; acid number, 0·48 to 1·30; ester number, 18·49 to 27·82; ester number after acetylation, 28·64 to 46·24. Bark oil, yield, 0·14%; D 0·8621; n_D^{15} 1·4716; α_D^{20} $+1·10°$; acid number, 0·60; ester number, 3·22; ester number after acetylation, 9·53. The approximate percentage composition of the oils was:

	Leaf and twig oil.	Bark oil.
Furfuraldehyde	trace	trace
l-α-Pinene	12—16	75—85
d-Sylvestrene, *d*-Limonene	54—58	—
Dipentene	—	5—6
Bornyl acetate	8	1
Free borneol	4	2
"Libocedrene"	6—7	—
"Green oil"	2	3
Losses	6	6

Libocedrene is a sesquiterpene, D 0·9292, b. p. 260—280°, n_D^{20} 1·4994, α_D^{20} +6·4°; it yielded a hydrochloride, m. p. 132—133°.

W. P. S.

Lacustrine Ambers. L. Reutter (*Compt. rend.*, 1916, **162**, 421—423).—An attempt to determine the source of origin of a specimen of amber from its chemical behaviour. Three German specimens from the Baltic Sea and two Italian specimens, one from Sicily and the other from Bologna, were examined in detail. All these ambers contained very small quantities of sulphur and also some borneol.

The residues from the Italian ambers, after extraction with ether and alcohol, are amorphous, whilst those from the German ambers are crystalline. The alcoholic and ethereal extracts from the Italian ambers, when treated with fuming nitric acid, give off nitrous fumes, the acid layer becoming coloured green, but there is no deposit. The extracts from the German ambers, under similar conditions, give a white, crystalline precipitate, m. p. 180—185°, but no green coloration or liberation of nitrous fumes is noticeable. The Italian ambers have a slightly higher melting point than the German ambers, and their alcoholic extracts are darker yellow in colour. The residues, after extracting the ambers with ether and alcohol, when warmed with aqueous potassium hydroxide, give respectively brown and yellow solutions, which, when acidified with sulphuric acid, give respectively brownish-yellow and white, crystalline precipitates, the former being soluble and the latter insoluble in ether. These precipitates consist of resin acids, with varying amounts of succinic acid. The Italian ambers contain from 1 to 16 per cent. of succinic acid, whilst the German ambers contain from 65 to 80 per cent. of succinic acid. Various museum specimens of amber have been examined and classified as to their origin.

W. G.

Some Ebullioscopic Determinations of Molecular Weights in Pyridine. A. L. van Scherpenberg (*Rec. trav. chim.*, 1916, **35**, 346—364).—The molecular weights of a number of organic plant products have been determined by the ebullioscopic method in a Beckmann apparatus, using specially purified pyridine, for which the constant, as obtained by determinations using diphenylamine and benzil as solutes respectively, was found to be $K=26·87$.

Euxanthogen, isolated from the bark and leaves of *Mangifera indica* by Wiechowsky (compare *Lotos*, 1908, **56**, 61), was found to have the molecular formula, $C_{19}H_{18}O_{11}$, this being the empirical formula given by Wiechowsky (*loc. cit.*). The values obtained for the tannin of tea (*Thea chinensis*, Sims.) were not absolute, but were in agreement with those obtained by Nanninga, using Lansberger's method with acetone as solvent.

The mean value obtained for mangostin (compare Hill, T., 1915, **107**, 595) corresponded with a molecular weight, 427·2, this being considerably higher than the values obtained by Nydam (compare *Zeitsch. physikal. Chem.*, 1904, **44**, 173), using respectively ethylene

dibromide, benzene, and nitrobenzene as solvents. Similarly, high results were obtained for methylmangostin (compare Kostanecki and Tambor, A., 1902, i, 553). W. G.

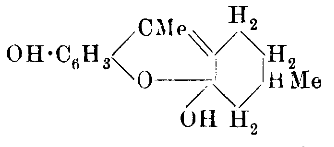
Oxonium Compounds. II. Oxonium Compounds with Reactive Methylene. W. BORSCHE and K. WUNDER (*Annalen*, 1916, **411**, 38—72. Compare A., 1912, i, 891).—In the earlier paper it was pointed out that in pyrylium salts the methylene group attached to the carbon atom adjacent to the quadrivalent oxygen atom is able to enter into condensations. An account of the condensations of many of these salts with aldehydes and nitrous acid, as being the only reagents for active methylene which can be applied in strongly acid solutions, is now given. Characteristic of the products with aldehydes are their double salts with ferric chloride, which crystallise without water of crystallisation or excess of acid.

I. *Starting Materials.*—For 2-methylbenzopyrylium chloride, see Decker and von Fellenberg (A., 1907, i, 1064) and for 3-methyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride, see earlier paper. 5-Methylsalicylaldehyde was condensed with 3-methyl*cyclo*hexanone by the method previously described, and *4-5′-methylsalicylidene-1-methyl*cyclo*hexan-3-one*, $OH\cdot C_6H_3Me\cdot CH{:}C_6H_7O\cdot Me$, was obtained in yellow needles or stout prisms, m. p. 142°. This was dissolved in a saturated solution of hydrogen chloride in glacial acetic acid, and then *3 : 13-dimethyl-1 : 2 : 3 : 4-tetrahydroxanthylium ferrichloride*, $C_6H_3Me{<}{}^{CH}_{OCl}{\gg}C_6H_7Me,FeCl_3$, was precipitated in long, bright red needles, m. p. 104—105°. Similarly, 5-chlorosalicylaldehyde was condensed with 3-methyl*cyclo*hexanone to form *4-5′-chlorosalicylidene-1-methyl*cyclo*hexan-3-one*, stout, yellow needles, m. p. 153°, and this was converted into *13-chloro-3-methyl-1 : 2 : 3 : 4-tetrahydroxanthylium ferrichloride*, $C_{14}H_{14}OCl_2,FeCl_3$, which crystallised in long, lustrous, green needles, m. p. 110—111°.

Other benzopyrylium salts were obtained by condensing polyhydric phenols with $\alpha\gamma$-diketones, for example, 9-hydroxy-2 : 4-dimethylbenzopyrylium chloride (Bülow and Wagner, A., 1901, i, 400). New salts were prepared by this method, as follows: Resorcinol and α-acetyl*cyclo*hexanone yielded *12-hydroxy-10-methyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride*, $OH\cdot C_6H_3{<}{}^{CMe}_{OCl}{\gg}C_6H_8$, in greenish-yellow needles, m. p. 167—169°, which formed a yellow *ferrichloride*, $3C_{14}H_{15}O_2Cl,2FeCl_3$, m. p. 161—162°, and a *picrate*, $C_{14}H_{15}O_2,C_6H_2O_7N_3$, in iridescent, brownish-yellow crystals, decomp. 170°. The pyrylium chlorides from acetyl*cyclo*hexanone and trihydric phenols were found to be too insoluble for the present investigation, but the following are briefly described: *11 : 12-dihydroxy-10-methyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride*, bright red needles, m. p. 250—251°, from pyrogallol; *12 : 13-dihydroxy-10-methyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride*, slender, yellow needles, m. p. 250°, from 1 : 3 : 4-trihydroxybenzene; *12 : 14-dihydr-*

oxy-10-*methyl*-1 : 2 : 3 : 4-*tetrahydroxanthylium chloride*, brilliant yellow crystals, m. p. 258—260°, from phloroglucinol.

Resorcinol was also condensed with 4-acetyl-1-methyl*cyclo*hexan-3-one to form 12-*hydroxy*-3 : 10-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroxanthylium chloride*, which crystallised in stellar aggregates of yellow needles, m. p. 180—182°, and formed a *ferrichloride*, $3C_{15}H_{17}O_2Cl,2FeCl_3$, in yellow leaflets, m. p. 155°. The salt was converted into the free *base* (annexed formula) by treatment with sodium acetate in the cold, and this was analysed as the *anhydride*. The



methyl ether, from resorcinol methyl ether, formed a normal *ferrichloride*, $OMe\cdot C_6H_3<^{CMe}_{-OCl}>C_6H_7Me$, in slender, yellow needles, m. p. 101—102°.

II. *Condensations of the Oxonium Chlorides with Aromatic Aldehydes.*—2-Methylbenzopyrylium chloride was condensed with piperonaldehyde by adding the latter to a solution of *o*-hydroxybenzylideneacetone in glacial acetic acid saturated with hydrogen chloride. The product, 2-*methylenedioxystyrylbenzopyrylium chloride*, $C_6H_4<^{CH:CH}_{-----OCl}>C\cdot CH:CH\cdot C_6H_3:O_2:CH_2,2H_2O$, was obtained in lustrous, green crystals, decomp. 195—200°, which formed a *ferrichloride*, $C_{18}H_{13}O_3Cl,FeCl_3$, m. p. 208°. 3-Methyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride was similarly applied in the form of a solution of the salicylidene-1-methyl*cyclo*hexan-3-one in acetic acid saturated with hydrogen chloride, and the following compounds were isolated: 4-*benzylidene*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydroxanthylium ferrichloride*, $C_{21}H_{19}OCl,FeCl_3$, orange needles, m. p. 129—130°; the 4-*cinnamylidene* compound, $C_{23}H_{21}OCl,FeCl_3$, coppery leaflets, decomp. 203—204°; the 4-p-*hydroxybenzylidene* compound, $C_{21}H_{19}O_2Cl,2H_2O,HCl$, bluish-green, shimmering needles, m. p. 127—128° (decomp.), *ferrichloride*, $C_{21}H_{19}O_2Cl,FeCl_3$, dark red granules, m. p. 153—154°; the 4-p-*methoxybenzylidene* compound, $C_{22}H_{21}O_2Cl,FeCl_3$, dark red needles, m. p. 177° (decomp.); the 4-*piperonylidene* compound, $C_{22}H_{19}O_3Cl,FeCl_3$, greenish-black, flat needles, m. p. 166—167°; the 4-o-p-*dihydroxybenzylidene* compound, $2C_{21}H_{19}O_3Cl,H_2O$, dark reddish-green crystals, decomp. 188—189°; and the 4-p-*nitrobenzylidene* compound, $C_{21}H_{18}O_3NCl,FeCl_3$, slender, orange-red needles, m. p. 144—145°.

3 : 13-Dimethyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride, applied in the form of a solution of 4-5′-methylsalicylidene-1-methyl*cyclo*hexan-3-one, gave the following compounds: 4-5′-*methylsalicylidene*-3 : 13-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroxanthylium chloride*, $(C_{23}H_{23}O_2Cl)_2,HCl$, dark red needles with green reflex, m. p. 154°, *ferrichloride*, $C_{23}H_{23}O_2Cl,FeCl_3$, dark greenish-black needles, m. p. 179—180°; the 4-p-*hydroxybenzylidene* compound, $C_{22}H_{21}O_2Cl$, golden-green crystals, m. p. 175°; and the 4-*piperonylidene* compound, $C_{23}H_{21}O_3Cl,FeCl_3$, dark red needles with green lustre, m. p. 156—157°.

13-Chloro-3-methyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride, applied in the form of a solution of 4-5′-chlorosalicylidene-1-methyl*cyclo*hexan-3-one, yielded 13-*chloro*-4-*benzylidene*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydroxanthylium ferrichloride*, $C_{21}H_{18}OCl_2,FeCl_3$, brown crystals with green reflex, m. p. 140°; the 4-5′-*chlorosalicylidene compound*, $C_{21}H_{17}O_2Cl_3$, brassy crystals, decomp. 150°; and the 4-*piperonylidene* compound, $C_{22}H_{18}O_3Cl_2,FeCl_3$, greenish-golden crystals, decomp. 160°.

9-Hydroxy-2 : 4-dimethylbenzopyrylium chloride yielded 9-*hydroxy*-2-o-*hydroxystyryl*-4-*methylbenzopyrylium chloride*,

$$OH\cdot C_6H_3{<}\begin{matrix}CMe{:}CH \\ OCl{=}C\cdot CH{:}CH\cdot C_6H_4\cdot OH\end{matrix},\ \tfrac{1}{2}H_2O,$$

red granules, decomp. 189°; the 2-*methylenedioxystyryl* compound, $C_{19}H_{15}O_4Cl,H_2O$, dark red crystals, m. p. 215°, *ferrichloride*, $C_{19}H_{15}O_4Cl,FeCl_3$, very dark brown, decomp. 190°; and the 2-o-p-*dihydroxystyryl* compound, $C_{18}H_{15}O_4Cl,H_2O$, a metallic-green powder, m. p. 232°.

12-Hydroxy-10-methyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride formed a 4-p-*hydroxybenzylidene* compound, $C_{21}H_{19}O_3Cl,H_2O$, as a dark reddish-brown shale, m. p. 205—206°.

12-Hydroxy-3 : 10-dimethyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride yielded a 4-*salicylidene* compound, $C_{22}H_{21}O_3Cl,H_2O$, as a brilliant red powder, m. p. 247—248°; and two 4-o-p-*dihydroxybenzylidene* compounds, $2C_{22}H_{21}O_4Cl,2HCl,H_2O$, dark red powder, decomp. 210—211°, and $2C_{22}H_{21}O_4Cl,3H_2O$, a black, crystalline crust, m. p. 239° (decomp.).

III. *Nitrosation of the Oxonium Chlorides.*—A solution of 3-methyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride in glacial acetic acid saturated with hydrogen chloride yielded, with *iso*amyl nitrite, 4-*oximino*-3-*methyl*-1 : 2 : 3 : 4-*tetrahydroxanthylium chloride*,

$$C_6H_4{<}\begin{matrix}CH \\ OCl\end{matrix}{>}C_6H_5Me{:}N\cdot OH,H_2O,$$

radiating, pale yellow needles, decomp. 194—195°, which formed a *ferrichloride*, $C_{14}H_{14}O_2NCl,FeCl_3$, thin, dark yellow prisms. The corresponding *carbinol* apparently changed into an anhydride when left in a desiccator. An attempt was made to obtain a benzoate of this by treating it (or the chloride) with benzoyl chloride in pyridine, but the product proved to be γ-*coumarinyl*-α-*methylbutyronitrile*, $C_6H_4{<}\begin{matrix}CH{:}C\cdot CH_2\cdot CH_2\cdot CHMe\cdot CN \\ O{-}{-}{-}CO\end{matrix}$, a ring having been ruptured. The nitrile crystallised in nodules of needles, m. p. 116°, and was hydrolysed to the *acid*, $C_{14}H_{14}O_4$, white needles, m. p. 141—142°.

3 : 13-Dimethyl-1 : 2 : 3 : 4-tetrahydroxanthylium chloride formed a similar 4-*oximino*-compound, $C_{15}H_{16}O_2NCl,2H_2O$, yellow needles, m. p. 218—220° (decomp.) (*ferrichloride*, $C_{15}H_{16}O_2NCl,FeCl_3$, stout, yellowish-brown needles, decomp. 165°), and this was converted into

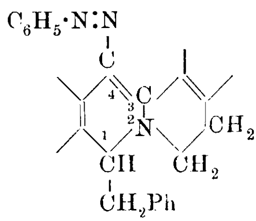
γ-5-*methylcoumarinyl-α-methylbutyronitrile*, white needles, m. p. 105—106°, and the corresponding *acid*,

$$C_6H_3Me<\begin{matrix}CH:C\cdot CH_2\cdot CH_2\cdot CHMe\cdot CO_2H,\\ O---CO\end{matrix}$$

a crystalline powder, m. p. 142—143°. J. C. W.

Berberine. III. Azo-derivatives of Dihydroberberine and 1-Alkyldihydroberberines. MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1916, **411**, 1—13. Compare A., 1913, i, 502; 1915, i, 982). —It has been shown that dihydroberberine and its 1-alkyl derivatives contain a very reactive hydrogen atom in position 4. The activity is now exemplified by the formation of many azo-compounds with diazonium salts, a property which is not shared by berberine or narcotine, although the latter has a reactive hydrogen atom (compare A., 1912, i, 490). The dihydroberberines are indifferent towards sodium, however.

The 1-benzyl derivative was examined more closely. 4-Benzeneazo-1-benzyldihydroberberine (annexed formula) is found to be rather sensitive towards reducing agents, although it does not behave like other azo-compounds, but yields 1-benzyldi- or even -tetra-hydroberberine. This is explained by the assumption that the compound is first reduced to a hydrazone, which then suffers hydrolysis, the conjugated system $-N:N\cdot C:C<$ changing into $-NH\cdot N:C\cdot CH<$.



A cold solution of 1-benzyldihydroberberine in 50% acetic acid was slowly added to a solution of benzenediazonium sulphate and the azo-compound was then precipitated by saturating the mixture with ammonia. 4-*Benzeneazo*-1-*benzyldihydroberberine*, $C_{33}H_{29}O_4N_3$, was obtained from a mixture of alcohol and chloroform in dark red, glistening, microscopic, rhombic tablets, m. p. 185°, and further characterised by a *hydrochloride*, yellowish-red, glistening tablets, decomp. 146°, a *sulphate*, decomp. about 180°, and a *methiodide*, deep red, microscopic tablets, decomp. 213°. When warmed with zinc dust and acetic acid for a few minutes, it yielded 1-benzyldihydroberberine, but the tetrahydro-base was also formed on prolonging the action. Electrolytic reduction gave a mixture of 1-benzyltetrahydroberberine and the more soluble, isomeric ψ-compound which is now described as a grey powder, m. p. 141—142° (compare A., 1913, i, 502).

4-*Benzeneazo*-1-*ethyldihydroberberine*, $C_{28}H_{27}O_4N_3$, was obtained as a crystalline powder with a coppery lustre, m. p. 216°. 4-p-*Sulphobenzeneazo*-1-*benzyldihydroberberine*, $C_{23}H_{28}O_4N_3\cdot SO_3H$, from sulphanilic acid, crystallised from glacial acetic acid in bundles of reddish-yellow spikelets, decomp. 274°. 4-α-*Naphthaleneazo*-1-*benzyldihydroberberine*, $C_{37}H_{31}O_4N_3$, formed a dark brown powder,

m. p. 218°, and the dark red, amorphous *β-naphthaleneazo*-compound yielded a reddish-yellow, crystalline *sulphate*, decomp. 191°. 4 : 4′-*Bisdiphenyleneazodi*-1-*benzyldihydroberberine*,

$$CH_2Ph\cdot C_{20}H_{17}O_4N\cdot (N_2)_2C_{12}H_8,$$

from benzidine, gave deep violet-red solutions in chloroform, and separated as a brownish-black powder, m. p. above 200°. 4-p-*Arsinobenzeneazo*-1-*benzyldihydroberberine*,

$$CH_2Ph\cdot C_{20}H_{17}O_4N\cdot N{:}N\cdot C_6H_4\cdot AsO_3H_2,$$

from sodium arsanilate (atoxyl) formed a reddish-yellow, crystalline powder and a deep red sodium salt. J. C. W.

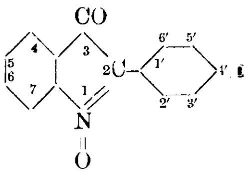
Preparation of *N*-Methyl Derivatives of Organic Bases. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 287802; from *J. Soc. Chem. Ind.*, 1916, **35**, 198).—Primary or secondary amines may be methylated by heating to a high temperature with formaldehyde in presence of some oxidisable organic compound (other than formic acid or formaldehyde). If the amine itself contains a readily oxidisable substituent, such as an alcohol radicle, it may be heated alone with formaldehyde, when simultaneous oxidation and methylation occur. Thus α-*N*-methylpyrrolidylpropan-α-one is obtained from diacetonemethylamine, methylpiperidine, etc. From α-pyrrolidylpropan-β-ol a methylated ketone is obtained, probably identical with the racemic form of the alkaloid hygrine.

G. F. M.

***N*-Alkylated Imino-ketones.** SYNTHETIC PATENTS Co. (U.S. Pat. 1158496; from *J. Soc. Chem. Ind.*, 1916, **35**, 275).—*N*-Alkylated imino-ketones are produced as the result of simultaneous oxidation and alkylation when heterocyclic imino-alcohols containing an exocyclic carbinol group are heated with an aldehyde. Thus α-pyrrolidylpropan-α-ol, when heated in hydrochloric acid solution with 40% formaldehyde for four hours at 115—120°, is converted into α-*N*-methylpyrrolidylpropan-α-one, which is separated by addition of alkali and extraction with ether. It is an oil, b. p. 70—75°/12 mm. The products, generally, are oils with an alkaline reaction, soluble in water, alcohol, and ether, and yield crystalline picrates and oximes. G. F. M.

Preparation of Sodium Oxindole-*p*-sulphonate. J. HAUSMANN (D.R.-P. 289028; from *J. Soc. Chem. Ind.*, 1916, **35**, 353).—Phenylacetic acid is sulphonated at 70—150° with three to five times its weight of sulphuric acid (D 1·84), the sulphonic acid is nitrated, and the nitrosulphonic acid reduced. The addition of a mineral acid to the reaction product, if alkaline, causes the precipitation of a mixture of *oxindole*-5-*sulphonic acid* with a smaller proportion of p-*aminosulphophenylacetic acid*, which can be separated by reason of their different solubilities in water. The sodium salt of the former acid gives with nitric acid isatoxime-7-sulphonic acid, and that of the latter a diazo-compound. Both compounds serve for the preparation of dyes. G. F. M.

Photochemical Synthesis of Indole Derivatives. PAUL PFEIFFER [with S. BRAUDE, R. FRITSCH, W. HALBERSTADT, G. KIRCHHOFF, J. KLÉBER, and P. WITTKOP] (*Annalen*, 1916, **411**, 72—158. Compare preliminary note, A., 1912, i, 618).—The new compounds described in this paper are derived from an unknown isomeride of isatin, to which, for reasons that are given, the structure $C_6H_4<{CO \atop NO}>CH$ must be assigned. The "isatogenates" obtained in 1880 by Baeyer are allied to these compounds, and, therefore, it is proposed to call the basal substance "isatogen." The notation which is adopted will appear from the annexed formula for "2-phenylisatogen." These isatogens have especial interest because of their pronounced quinonoid character. In fact, they are the first genuine meta-quinonoid substances.



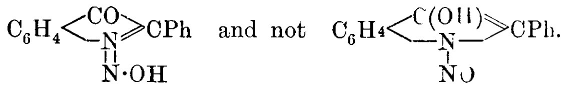
The starting materials for the photochemical synthesis of these isatogens are the *o*-nitrostilbenes. The dichlorides of these lose the elements of hydrogen chloride when warmed with pyridine, forming monochlorostilbenes, and when solutions of these or the original dichlorides in pyridine (or quinoline, but not other solvents) are exposed to the light, highly-coloured compounds are formed, with the elimination of the remaining hydrogen chloride. These are not the *o*-nitrotolanes, for they are darker in colour and otherwise quite distinct. They are isomeric with the *o*-nitrotolanes, however, and these change very readily into the highly coloured substances in pyridine solution, even in the dark. For the transformation of the chlorostilbenes light, and especially short-waved light, is essential, but the mechanism of the change into the chlorine-free compounds is not known.

The evidence is in favour of the assumption that the new compounds, the isatogens, are formed by the closing of a ring between the 2-carbon bridge and the *o*-nitro-group. Only *o*-nitrostilbenes react in this way, and reduction with zinc dust and acetic acid leads to the formation of phenylindoxyls, acetates of which may be prepared. It can also be shown that the isatogens contain two reactive groups, >C:O and >N:O ("nitrone"), for they all yield two oximes, pale yellow and orange. The orange oxime is the C-oxime, for the simple 2-phenylisatogen yields the oxime that Angeli and Angelico (A., 1907, i, 153) obtained by the action of amyl nitrite on 1-hydroxy-2-phenylindole, thus:

$$C_6H_4<{CO \atop NO}>CPh \longrightarrow C_6H_4<{C(:NOH) \atop NO}>CPh \longleftarrow C_6H_4<{CH \atop N(OH)}>CPh.$$

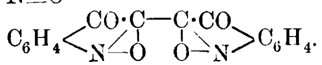
These oximes yield aminophenylindoles, for example, 3-amino-2-phenylindole, on reduction, but the pale yellow oximes yield phenylindoxyls. The paler oximes cannot, therefore, be desmotropes of the orange ones, and they must be regarded as N-oximes. The acetates of these oximes yield phenylindoxyls, and not acetylphenylindoxyls, on reduction, and therefore the oximes must be true

oximes, and not the tautomeric nitroso-compounds, that is, for example:

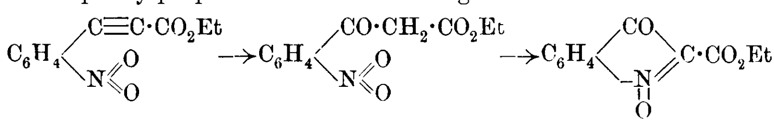


The isatogens are all typical quinonoids. They form, for example, typical quinhydrones. The simple isatogen is related to indole like benzoquinone to benzene, as the above formula expresses.

The isatogens which Baeyer obtained by the action of concentrated sulphuric acid on ethyl *o*-nitrophenylpropiolate and *oo'*-dinitrodiphenyldiacetylene were formulated by him as follows: ethyl isatogenate, $C_6H_4<\substack{CO\cdot C\cdot CO_2Et \\ N\angle O}$, and di-isatogen,



These old formulæ do not account for the colours of these compounds, for the keto-group is not paired with another chromophore. The new quinonoid formulation, for example, $C_6H_4<\substack{CO \\ NO}>C\cdot CO_2Et$, would be more in accordance with the facts, and seems to be all the more plausible, since Baeyer's compounds can be obtained by the same "photochemical-pyridine" method. Thus, methyl and Baeyer's ethyl isatogenates can be obtained by dissolving the *o*-nitrophenylpropiolates in pyridine, just as *a*-phenylisatogen can be obtained from *o*-nitrotolane. This formulation also accounts for the mechanism of Baeyer's reaction and for the fact that *o*-nitrotolanes cannot be isomerised by sulphuric acid. Water is first taken up at the triple linking, the oxygen being attached at the carbon atom carrying the less negative residue, and subsequent condensation can only take place if the nitro-group can enter into the formation of a 5-ring with the newly-formed methylene. Thus, ethyl *o*-nitrophenylpropiolate reacts according to the scheme:



whereas 2:4-dinitrotolane only forms 2:4-dinitrodeoxybenzoin, $C_6H_4(NO_2)_2\cdot C\!:\!CPh \longrightarrow C_6H_4(NO_2)_2\cdot CH_2\cdot COPh$.

The introductory chapter in the original also devotes several pages to a general summary of the preparations and properties of the required stilbenes and the phenylisatogens and isatogenates.

A. *2-Phenylisatogen and its Mono-substituted Products.*—I. 2:4-Dinitrostilbene (Thiele and Escales, A., 1901, i, 689) was reduced to 2-nitro-4-aminostilbene, and this was converted into 2-nitrostilbene by Sachs and Hilpert's method (A., 1906, i, 242). This was then saturated with chlorine in carbon

disulphide, and the product was separated by repeated crystallisations from methyl alcohol into the *a-dichloride*, faintly yellow, compact crystals, m. p. 122°, and the *β-dichloride*,

$$NO_2\cdot C_6H_4\cdot CHCl\cdot CHPhCl,$$

stout, rhombic crystals, m. p. 76—79°, both of which were readily converted by the action of aqueous-alcoholic sodium hydroxide into 2-*nitrotolane*, $NO_2\cdot C_6H_4\cdot C\colon CPh$, which was obtained in yellow, prismatic needles or tablets, m. p. 50—52°. By exposing a pyridine solution of the crude dichloride or the tolane to the light, the colour speedily deepened, and ultimately 2-*phenylisatogen* was deposited. The pure substance formed brilliant, deep orange-red leaflets, m. p. 186—187°, and was converted into the above-mentioned mixture of oximes by boiling with alcoholic hydroxylamine hydrochloride. These were separated by fractionation from glacial acetic acid, the C-oxime crystallising first in glistening, orange leaflets, m. p. 236° (compare Angeli and Angelico, *loc. cit.*), followed by the N-*oxime*, $C_{14}H_{10}O_2N_2$, in pale yellow prisms, m. p. 167—168°.

II. 6-*Nitro*-2-*phenylisatogen*.—This was originally prepared by exposing a pyridine solution of *a*-chloro-2 : 4-dinitrostilbene to the light. It may also be obtained in this way from the dichloride or by boiling or illuminating a pyridine solution of 2 : 4-dinitrotolane (Pfeiffer and Kramer, A., 1914, i, 32). The mixture of oximes was separated by means of aqueous ammonia, in which the N-oxime is almost insoluble. The N-*oxime*, $NO_2\cdot C_6H_3{<}\begin{matrix}\text{—CO—}\\ \text{N(NOH)}\end{matrix}{>}CPh$, crystallised with $2CH_3\cdot CO_2H$ in flat needles, but lost the solvent on exposure, and then had m. p. 183° (decomp.); the *acetyl* derivative formed slender, pale yellow needles, m. p. 136—137°. The C-*oxime*, $NO_2\cdot C_6H_3{<}\begin{matrix}\text{C(NOH)}\\ \text{——NO}\end{matrix}{>}CPh$, crystallised, on cooling a solution in glacial acetic acid slowly, in deep orange-red leaflets, but on rapid cooling, in orange-yellow leaflets, m. p. 250° (decomp.); the *acetyl* derivative formed orange-red, glistening leaflets, m. p. 226°.

III. 4-*Nitro*-2-*phenylisatogen*.—2 : 6-Dinitrostilbene was prepared by condensing 2 : 6-dinitrotoluene with benzaldehyde, in pale yellow needles, m. p. 114° (compare Pfeiffer and Monath, A., 1906, i, 413). When a suspension in carbon disulphide was treated with chlorine, it gradually dissolved, and then deposited the *a-dichloride*, $C_6H_3(NO_2)_2\cdot CHCl\cdot CHPhCl$, in glistening, pale yellow leaflets, m. p. 204—205°, whilst a chloroform suspension yielded the *β-dichloride* in well-developed tablets, m. p. 161°. The *dibromide* was obtained in stout, transparent, pale yellow tablets, m. p. 146—147°. The dihaloids were boiled with pyridine and converted into *a-chloro*-2 : 6-*dinitrostilbene*, $C_6H_3(NO_2)_2\cdot CCl\colon CHPh$, pale yellow needles, m. p. 100—101°, and *a-bromo*-2 : 6-*dinitrostilbene*, glistening, yellow, rhombic crystals, m. p. 111°. After leaving a pyridine solution of the dichloride for some weeks in the sunlight, 4-*nitro*-2-*phenylisatogen* was obtained in large, brilliant, bright red leaflets, m. p. 194°.

IV. 2′-*Nitro*-2-*phenylisatogen*.—2 : 2′-Dinitrostilbene was converted into the dichloride (two forms were observed, m. p. 152—153°

and m. p. 203°), and this into the α-chlorostilbene by boiling with pyridine (Pfeiffer, 1912). This yielded 2′-*nitro*-2-*phenylisatogen* in yellowish-orange leaflets, m. p. 202—203°.

V. 6-*Cyano*-2-*phenylisatogen* was obtained from α-chloro-2-nitro-4-cyanostilbene (*ibid.*) in glistening,yellowish-orange leaflets, m. p. 227°. It was converted into the two oximes, which were separated by means of ammonia. The insoluble N-*oxime*, $C_{15}H_9O_2N_3$, was obtained in glistening, yellow leaflets, m. p. 212—213°, converted into the *acetyl* derivative, pale pink needles, m. p. 151—151·5°, and both were reduced by means of zinc dust and acetic acid to 2-cyanophenylindoxyl. The C-*oxime* formed glistening, orange leaflets, m. p. 246°. The 6-cyanophenylisatogen was also reduced by means of zinc dust and acetic acid to 6-*cyano*-2-*phenylindoxyl*, $CN{\cdot}C_6H_3{<}{\begin{smallmatrix}C(OH)\\NH\end{smallmatrix}}{>}CPh$, which crystallised, with $1H_2O$, in silvery needles which lost their water at 90—100°, and had m. p. 215°. Solutions in most organic media showed a brilliant blue fluorescence. The *acetyl* derivative formed glistening, white needles, m. p. 190—191°. On cooling a solution of 6-cyanophenylindoxyl (3 grams) and 6-cyanophenylisatogen (0·7 gram) in glacial acetic acid, a *quinhydrone* separated in glistening, black needles, m. p. 185—186°.

VI. *Methyl* 2-*phenylisatogen*-6-*carboxylate* was obtained by saturating an alcoholic solution of the acid (see below) with hydrogen chloride, in brilliant, orange leaflets, m. p. 132—133°.

VII. *Ethyl* 2-*phenylisatogen*-6-*carboxylate*, m. p. 138°, was prepared from the acid, or by saturating an alcoholic solution of the above 6-cyanophenylisatogen with hydrogen chloride, or by illuminating a pyridine solution of ethyl α-chloro-2-nitrostilbene-4-carboxylate (*ibid.*) or a solution of the corresponding *dichloride*, $CO_2Et{\cdot}C_6H_3(NO_2){\cdot}CHCl{\cdot}CHPhCl$, which was obtained in white needles, m. p. 88·5°, by the action of hydrogen chloride on an alcoholic solution of the nitrile (*ibid.*). The oximes of the ester were separated as usual. The predominant N-*oxime*, $C_{17}H_{14}O_4N_2$, formed colourless, slender needles, m. p. 191°, and its *acetyl* derivative had m. p. 134°. It was reduced to *ethyl* 2-*phenylindoxyl*-6-*carboxylate*, which formed glistening, yellow leaflets, m. p. 183—188° (decomp.), fluoresced strongly in solution, and yielded an *acetate*, $C_{19}H_{17}O_4N$, glistening needles, m. p. 187—190°.

VIII. 2-*Phenylisatogen*-6-*carboxylic acid* was obtained from α-chloro-2-nitrostilbene-4-carboxylic acid (*ibid.*) as an orange powder, m. p. 231—233°, which formed a *pyridine* salt, orange-red needles, m. p. 150—151°, and molecular *compounds* with acetic and propionic acids.

B. *Disubstituted Phenylisatogens.*—I. 6 : 3′-*Dinitro*-2-*phenylisatogen.*—2 : 4-Dinitrotoluene was heated with *m*-nitrobenzaldehyde and a little piperidine at 185°, and thus condensed to 2 : 4 : 3′-*trinitrostilbene*, which formed yellow needles, m. p. 182—183°. This was converted into the *dichloride*, transparent prisms, m. p. 168°, and *dibromide*, compact, pale yellow

crystals, m. p. 190—191°. The dichloride was transformed by boiling with pyridine into *α-chloro-2 : 4 : 3′-trinitrostilbene*,

$$C_6H_3(NO_2)_2\cdot CCl{:}CH\cdot C_6H_4\cdot NO_2,$$

pale yellow needles, m. p. 164°, and, by the above method into *2 : 3′-dinitro-2-phenylisatogen*, orange needles, m. p. 234°.

II. *6-Nitro-2-p-tolylisatogen*.—2 : 4-Dinitrotoluene was condensed with *p*-tolualdehyde to form *2 : 4-dinitro-4′-methylstilbene*, which crystallised in glistening, yellow leaflets, m. p. 197°. Two *dichlorides* of this were obtained, the α- in short, prismatic needles, m. p. 167—167·5°, and the β- in long, asbestos-like needles, m. p. 155°. The crude mixture of these was converted into *α-chloro-2 : 4-dinitro-4′-methylstilbene*, $C_6H_3(NO_2)_2\cdot CCl{:}CH\cdot C_6H_4Me$, slender, yellow tablets or needles, m. p. 136°, and into *6-nitro-2-p-tolylisatogen*, violet-red leaflets, m. p. 212°.

III. *6-Nitro-4′-methoxy-2-phenylisatogen*.—Anisaldehyde and 2 : 4-dinitrotoluene yielded *2 : 4-dinitro-4′-methoxystilbene*, in stout, orange-red crystals, m. p. 163°, and from the honey-like dichloride of this, *6-nitro-4′-methoxy-2-phenylisatogen* was obtained, in glistening, brownish-violet leaflets, m. p. 248°, which were not quite free from chlorine.

IV. *6-Nitro-4′-acetoxy-2-phenylisatogen*.—2 : 4-Dinitrotoluene was carefully heated with *p*-hydroxybenzaldehyde and piperidine, and then the mass was warmed with acetic anhydride. *2 : 4-Dinitro-4′-acetoxystilbene* was isolated in yellow needles, m. p. 148°, and converted into the *dichlorides*, α-, m. p. 158°, β-, m. p. 125—130°, and then into *6-nitro-4′-acetoxy-2-phenylisatogen*, orange leaflets, m. p. 235°.

V. *6-Nitro-4′-α-methylbutyroxy-2-phenylisatogen*.—*2 : 4-Dinitro-4′-hydroxystilbene* was prepared by the direct union of 2 : 4-dinitrotoluene with *p*-hydroxybenzaldehyde, or, better, by the hydrolysis of the above acetyl derivative, in orange leaflets from aqueous alcohol or deep red granules from xylene, m. p. 162°. This was acylated by means of α-methylbutyryl chloride (from commercial methylethylmalonic acid), and the *2 : 4-dinitro-4′-α-methylbutyroxystilbene*, $C_6H_3(NO_2)_2\cdot CH{:}CH\cdot C_6H_4\cdot O\cdot CO\cdot CHMeEt$, so obtained, in opalescent, yellow leaflets, m. p. 123°, was converted into an oily dichloride and then into *6-nitro-4′-α-methylbutyroxy-2-phenylisatogen*, glistening, red leaflets, m. p. 216°.

The 2 : 4-dinitro-4′-hydroxystilbene was also benzoylated, and the *benzoate*, m. p. 170°, was converted into the dichloride and into *6-nitro-4′-benzoyloxy-2-phenylisatogen*,

$$NO_2\cdot C_6H_3{<}^{CO}_{NO}{>}C\cdot C_6H_4\cdot OBz,$$

bright red leaflets, m. p. 252°.

VI. *6-Nitro-4′-hydroxy-2-phenylisatogen* itself was obtained by hydrolysing the above acetate with methyl-alcoholic potassium carbonate, in glistening, deep violet leaflets, m. p. 235—236° (decomp.).

VII. *6-Nitro-2-phenylisatogen-4′-sulphonic Acid*.—*α-Chloro-2 : 4-dinitrostilbene-4′-sulphonic acid*, $C_6H_3(NO_2)_2\cdot CCl{:}CH\cdot C_6H_4\cdot SO_3H$,

was prepared by dissolving the unsulphonated compound in concentrated sulphuric acid, in pale yellow crystals, and converted into 6-*nitro-2-phenylisatogen-4′-sulphonic acid*,

$$NO_2\cdot C_6H_3<\substack{CO \\ NO}>C\cdot C_6H_4\cdot SO_3H,$$

fiery-red leaflets, which forms a red *pyridine* salt.

VIII. 6-*Cyano*-2-p-*tolylisatogen*.—*o*-Nitro-*p*-toluonitrile and *p*-tolualdehyde were condensed to form 2-*nitro*-4-*cyano*-4′-*methylstilbene*, in flat, yellow needles, m. p. 170°, and this was converted into the *dichlorides* (α-, transparent, prismatic needles, m. p. 175—176°; β-, fibrous needles, m. p. 130—131°). These were transformed into α-*chloro*-2-*nitro*-4-*cyano*-4′-*methylstilbene*,

$$NO_2\cdot C_6H_3(CN)\cdot CCl{:}CH\cdot C_6H_4Me,$$

yellow leaflets, m. p. 133—134°, and into 6-*cyano*-2-p-*tolylisatogen*, red leaflets, m. p. 249°. The original cyanostilbene was hydrolysed by alcoholic hydrogen chloride to *ethyl* 2-*nitro*-4′-*methylstilbene*-4-*carboxylate*, $CO_2Et\cdot C_6H_3(NO_2)\cdot CH{:}CH\cdot C_6H_4Me$, long, yellow needles, m. p. 99—100°.

IX. 6-*Cyano*-4′-*methoxy*-2-*phenylisatogen*.—2-*Nitro*-4-*cyano*-4′-*methoxystilbene* was obtained by condensing *o*-nitro-*p*-toluonitrile with anisaldehyde (see this vol., i, 24), converted into the *dichloride*, very pale yellow crystals, m. p. 128—130°, and this into 6-*cyano*-4′-*methoxy*-2-*phenylisatogen*, lustrous, brownish-violet crystals, m. p. 257°. This was reduced by means of zinc dust and acetic acid to 6-*cyano*-4′-*methoxy*-2-*phenylindoxyl*,

$$CN\cdot C_6H_4<\substack{C(OH) \\ NH}>C\cdot C_6H_4\cdot OMe,$$

colourless needles, m. p. 203° (decomp.), which fluoresced strongly in solution and formed an *acetyl* derivative, m. p. 204°.

C. *Derivatives of Isatogenic Acid*.—I. *Methyl Isatogenate*.—*o*-Nitrophenylpropiolic acid was prepared by a convenient method from αβ-dibromo-*o*-nitrophenylpropionic acid, and converted into the *methyl* ester, $NO_2\cdot C_6H_4\cdot C{:}C\cdot CO_2Me$, very pale yellow leaflets, m. p. 87—88°, and this was transformed into the isomeric *methyl isatogenate*, $C_6H_4<\substack{CO \\ NO}>C\cdot CO_2Me$, orange-yellow plates, m. p. 201°, by the agency of pyridine. The ester formed a C-*oxime*, pale yellow needles, m. p. 220—221° (decomp.).

II. *Ethyl Isatogenate*.—The preparation of ethyl *o*-nitrophenylpropiolate and its isomerisation by Baeyer's original method and by means of pyridine are described.

III. *Methyl* 6-*Nitroisatogenate*.—*op*-Dinitrocinnamic acid was prepared from *op*-dinitrobenzaldehyde and found to yield a molecular *compound* with benzene. The acid was converted into the *methyl* ester, pale yellow, flat needles, m. p. 86—88°, then into *methyl* αβ-*dichloro*-β-op-*dinitrophenylpropionate*, m. p. 120°, and this into *methyl* α-*chloro*-op-*dinitrocinnamate*,

$$C_6H_3(NO_2)_2\cdot CH{:}CCl\cdot CO_2Me,$$

m. p. 125—126°. The original cinnamic acid was also brominated (*methyl* αβ-*dibromo*-β-op-*dinitrophenylpropionate* has m. p. 126°) and then dissolved in 1% aqueous sodium hydroxide, and thus con-

verted into op-*dinitrophenylpropiolic acid*, flat, pale yellow needles, m. p. 129° (crystallises with $1C_6H_6$). The *methyl* ester of this, very long, thin needles, m. p. 103·5°, reacted violently with pyridine, but by careful manipulation in the cold it was transformed into the isomeric *methyl* 6-*nitroisatogenate*, $NO_2\cdot C_6H_3{<}^{CO}_{NO}{>}C\cdot CO_2Me$, golden-yellow leaflets, m. p. 181°. J. C. W.

Production of Derivatives of 4-Hydroxycarbostyril. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 287803; from *J. Soc. Chem. Ind.*, 1916, **35**, 170).—*N*-Substituted alkyl or aryl derivatives of anthranilic acid are converted on heating into derivatives of 4-hydroxycarbostyril; thus phenylanthranilic acid gives 4-hydroxy-1-phenylcarbostyril on warming with acetic anhydride. G. F. M.

Preparation of 4-Cyano-2-arylquinolines. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P. 288243; from *J. Soc. Chem. Ind.*, 1916, **35**, 384).—The amides of 2-arylquinoline-4-carboxylic acids lose water when heated above their melting points, and the corresponding nitriles are formed. Details of the preparation of 4-*cyano*-2-*phenylquinoline* are given. From these cyano-compounds other therapeutically valuable derivatives can be produced. G. F. M.

Preparation of Quinoline Derivatives containing Iodine. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 288303; from *J. Soc. Chem. Ind.*, 1916, **35**, 384).—Iodised quinoline derivatives are obtained if in the usual methods for the preparation of derivatives of 2-phenylquinoline-4-carboxylic acid an iodine compound of an aromatic amine, of an aromatic aldehyde, or of acetophenone is used. The iodo-compounds are tasteless, and are of value therapeutically in the treatment of gout. As examples, the 4-*carboxylic acids* of 6-*iodo*-2-*phenylquinoline*, 2-p-*iodophenylquinoline*, and 6-*methoxy*-2-p-*iodophenylquinoline* are mentioned. G. F. M.

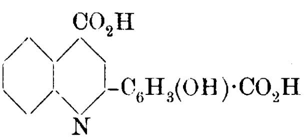
Preparation of Liquid Esters of 2-Phenylquinoline-4-carboxylic Acid and its Derivatives. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 287959; from *J. Soc. Chem. Ind.*, 1916, **35**, 384).—iso*Amyl* 2-*phenylquinoline*-4-*carboxylate* and its derivatives, prepared in the usual way, are valuable therapeutically on account of their oily nature and the ease with which they are absorbed by the skin. G. F. M.

Preparation of Amino-derivatives of 2-Phenylquinoline-4-carboxylic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 287804; from *J. Soc. Chem. Ind.*, 1916, **35**, 198).—Amino-derivatives of 2-phenylquinoline-4-carboxylic acid are obtained when nitroisatin is condensed with acetophenone and the nitro-group is

reduced, or when isatin is condensed with acidylaminoacetophenones and the products are saponified. They are of therapeutic value because, unlike the parent substance, they do not cause the separation of uric acid in the system. G. F. M.

Preparation of Amino-derivatives of 2-Phenylquinoline-4-carboxylic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 288865; from *J. Soc. Chem. Ind.*, 1916, **35**, 384).—Amino-derivatives of 2-phenylquinoline-4-carboxylic acid are obtained by condensing isatin with aminoacetophenone instead of with its acidyl derivative, as in the chief patent (D.R.-P. 287804; preceding abstract). G. F. M.

Preparation of Hydroxyphenylquinolinedicarboxylic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Eng. Pat., 1914, 22828; from *J. Soc. Chem. Ind.*, 1915, **34**, 889).—Hydroxyphenylquinolinedicarboxylic acid (annexed formula) is obtained by heating 5-acetyl-2-hydroxybenzoic acid with isatoic acid in alkali hydroxide solution on a water-bath for eight hours. It is precipitated from the reaction product with hydrochloric acid, and purified through its sodium salt or ethyl ester (m. p. 103°). It forms a yellow powder, m. p. 283—284° (decomp.), sparingly, or not at all, soluble in most solvents. The sodium salt has a sweet taste, and becomes yellow on treatment with sodium hydroxide. An alternative method of preparing the acid consists in treating *p*-aldehydosalicylic acid with aniline and pyruvic acid in alcohol. G. F. M.



Manufacture of Hydroxyphenylquinolinedicarboxylic Acid and Derivatives thereof. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Eng. Pat., 1915, 15752; addition to Eng. Pat., 1914, 22828; from *J. Soc. Chem. Ind.*, 1916, **35**, 329).—A solution of an alkali carbonate or an alkaline earth may be used instead of alkali hydroxide, as prescribed in the original patent. Also derivatives of isatoic acid, such as its methyl or methylenedioxy-derivatives, and homologues of acetylsalicylic acid, such as acetoxytoluic acids, may be used. The latter are obtained by condensing acetyl chloride with *o*-, *m*-, or *p*-cresotic acid in presence of aluminium chloride and carbon disulphide. G. F. M.

Additive Compounds of *s*-Trinitrobenzene with Heterocyclic Compounds Containing Nitrogen in the Ring. SOSALE GARALAPURY SASTRY (T., 1916, **109**, 270—273).—An extension of the work of Sudborough and his collaborators (compare T., 1911, **99**, 209; 1910, **97**, 773, etc.) on the additive compounds produced by *s*-trinitrobenzene with various classes of aromatic compounds.

The following additive compounds are described: 8-*Methyltetrahydroquinoline*–s-*trinitrobenzene*, brownish-black needles, m. p. 113°. 6-*Methyltetrahydroquinoline*–s-*trinitrobenzene*, dark plates,

m. p. 102°. *Tetrahydro-α-naphthaquinoline–s-trinitrobenzene*, dark needles, m. p. 129—130°. *Tetrahydro-β-naphthaquinoline–s-trinitrobenzene*, black needles, m. p. 138—139°. 5-*Methyl*-5:10-*dihydroacridine–s-trinitrobenzene*, black needles, m. p. 117—118°. 1:3:5-*Trianilinobenzene–s-trinitrobenzene*, black needles or prisms, m. p. 160°. *Phenazine–s-trinitrobenzene*, yellow needles, m. p. 151—153°. *Azoxyanisole–s-trinitrobenzene*, golden-yellow plates, m. p. 92—93°. 1-*Phenylbenzylidene*-3-*methyl*-5-*pyrazolone–s-trinitrobenzene*, scarlet plates, m. p. 113—114°.

In all these additive compounds, the two constituents are present in equimolecular proportions. Other additive compounds, of which the composition is not stated, were obtained with trinitrobenzene and dihydrophenylacridine (black), *s*-diphenylcarbazide (orange needles), and tetrahydro*iso*quinoline (a resin). It is a point of interest that the additive compounds derived from substances containing the grouping $\cdot CH_2\cdot NH\cdot$ are almost black.

The 5-*methyl*-5:10-*dihydroacridine*, $C_6H_4{<}{\begin{smallmatrix}CHMe\\NH\end{smallmatrix}}{>}C_6H_4$, m. p. 125—126°, required for the above investigation was prepared by reduction of methylacridine in alcoholic solution with sodium amalgam; it gave an *acetyl* derivative, m. p. 162°. 1-*Phenylbenzylidene*-3-*methyl*-5-*pyrazolone* was obtained as red needles, m. p. 106—107°, by heating together molecular proportions of benzaldehyde and 1-phenyl-3-methyl-5-pyrazolone. D. F. T.

Preparation of Green Wool Dyes of the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.P. 287614; from *J. Soc. Chem. Ind.*, 1916, **35**, 171).—The 4-amino-1-arylaminoanthraquinone-3-sulpho-2′-carboxylic acids or their derivatives, when treated with condensing agents in such a way that the 3-sulphonic group remains intact, furnish the 4-amino-2:1-anthracridone-3-sulphonic acids which further sulphonated, if necessary, give green shades on wool, and may also be used for the preparation of other dyes. G. F. M.

Preparation of Oximinosulphazone. M. CLAASZ (D.R.-P. 288682; from *J. Soc. Chem. Ind.*, 1916, **35**, 356).—When sulphazone (A., 1912, i, 390) or one of its substitution products having a free 2-position is converted in the usual way at normal temperatures into the nitroso-compound, the nitroso-group enters the azine nucleus, whilst nitration leads to the entry of a nitro-group into the benzene nucleus. *Oximinosulphazone*, $C_6H_4{<}{\begin{smallmatrix}NH\cdot CO\\SO_2\cdot C{:}N\cdot OH\end{smallmatrix}}$, obtained by the action of sodium nitrite in acid solution, gives indigo-blue shades on iron-mordanted wool, cotton, and silk; on reduction, it is converted into 2-aminosulphazone. G. F. M.

Derivatives of Glyoxaline-4 (or 5)-formaldehyde and Glyoxaline-4 (or 5)-carboxylic Acid. A New Synthesis of Histidine. FRANK LEE PYMAN (T., 1916, **109**, 186—202).—Glyoxaline-4(or 5)-formaldehyde (Pyman, T., 1912, **101**, 542) is so stable towards oxidising agents that it can be obtained in more than 50% yield

by the oxidation of 4(or 5)-hydroxymethyleneglyoxaline with nitric acid; even with a large excess of nitric acid a considerable quantity of glyoxalineformaldehyde accompanies the glyoxaline-4(or 5)-carboxylic acid.

Glyoxalineformaldehyde, $\begin{matrix} NH\cdot CH \\ | \\ CH{=}N \end{matrix}\!\!>\!C\cdot CHO$, is stable in the air and does not reduce ammoniacal silver nitrate, but gives a white precipitate with this reagent; it forms a red dye with sodium diazobenzene-*p*-sulphonate, and yields a *phenylhydrazone*, prisms, m. p. 199—200° (corr.). When heated with a mixture of hippuric acid, sodium acetate, and acetic anhydride, a clear, fluid mass is obtained which subsequently deposits yellow, prismatic needles of 2-*phenyl*-4-[1-*acetylglyoxaline*-4(or 5)-*methylidene*]-*oxazolone*,

$$\begin{matrix} CPh{:}N \\ | \\ O{-}CO \end{matrix}\!\!>\!C{:}CH\cdot C\!<\!\begin{matrix} CH\cdot NAc \\ | \\ N{=}CH \end{matrix},$$

m. p. 191° (corr.); this is decomposed when heated with dilute mineral acids, formic and acetic acids being obtained, presumably accompanied by glyoxalinepyruvic acid, and when boiled with sodium carbonate solution undergoes scission of the acetyl group with formation of *α-benzoylamino-β-glyoxaline*-4(or 5)-*acrylic acid*, $\begin{matrix} NH\cdot CH \\ | \\ CH{=}N \end{matrix}\!\!>\!C\cdot CH{:}C(NHBz)\cdot CO_2H$, colourless needles (with $1H_2O$), m. p. 208° (corr.; decomp.), which reduces potassium permanganate solution in the cold, gives a deep red coloration in neutral solution with sodium diazobenzene-*p*-sulphonate, and forms a *hydrochloride*, prismatic needles, m. p. 229° (corr.; decomp.), and a *picrate*, rosettes of yellow prisms, m. p. 212° (corr.; decomp.).

By reduction in aqueous suspension with sodium amalgam, α-benzoylamino-β-glyoxaline-4(or 5)-acrylic acid is converted into *benzoyl*-r-*histidine*, $\begin{matrix} NH\cdot CH \\ | \\ CH{=}N \end{matrix}\!\!>\!C\cdot CH_2\cdot CH(NHBz)\cdot CO_2H$, hard, glistening prisms (with $1H_2O$, lost at 115°), m. p. 248° (corr., decomp; compare Pauly, A., 1910, i, 336), which does not readily reduce cold aqueous potassium permanganate and forms a deep red coloration with sodium diazobenzene-*p*-sulphonate; *hydrochloride*, hard, glistening prisms, m. p. 232° (corr.), with effervescence; *picrate*, feathery, yellow needles, m. p. 226° (corr., decomp.). Hydrolysis of this benzoyl derivative with aqueous hydrochloric acid yielded *r*-histidine identical with a specimen synthesised by an independent method (T., 1911, **99**, 1386).

When potassium cyanide is introduced into a solution of glyoxalineformaldehyde in aqueous sodium hydrogen sulphite, the unstable *cyanohydrin*, $\begin{matrix} NH\cdot CH \\ | \\ CH{=}N \end{matrix}\!\!>\!C\cdot CH(OH)\cdot CN$, rosettes of prismatic needles, m. p. 115° (corr., decomp.), is obtained, which by reduction with sodium amalgam and hydrochloric acid in nearly neutral solution can be converted into *β-hydroxy-β-glyoxaline*-4(or 5)-*ethylamine*, $\begin{matrix} NH\cdot CH \\ | \\ CH{=}N \end{matrix}\!\!>\!C\cdot CH(OH)\cdot CH_2\cdot NH_2$; this was sepa-

rated as the *dipicrate*, $C_5H_9ON_3,2C_6H_3O_7N_3,H_2O$, orange-yellow, hexagonal plates or serrated spikes, m. p. 225° (corr. decomp.); *dihydrochloride*, colourless needles, m. p. 216° (corr. decomp.), gives a deep red colour with sodium diazobenzene-*p*-sulphonate; *platinichloride*, microscopic, orange prisms with $3H_2O$, decomp. 225—244°. A comparison of the physiological action of this base with that of 4(or 5)-β-aminoethylglyoxaline shows that the introduction of the hydroxyl group has diminished the physiological activity.

Glyoxaline-4(or 5)-carboxylic acid (compare Knoop, A., 1907, i, 788; Windaus and Ullrich, A., 1914, i, 662) crystallises in needles, m. p. 275° (corr.), with effervescence, if gradually heated from 100°, but m. p. 284° (corr.) if heated gradually from 270°; it forms a crystalline *sodium* salt; *hydrochloride*, clusters of microscopic prisms, m. p. 262° (corr.), with effervescence; *nitrate*, prisms, m. p. 200°, with subsequent re-solidification and fusion near 270°; *picrate*, plates with $1\frac{1}{2}H_2O$, m. p. 195—215° with effervescence; *ethyl* ester, plates, m. p. 162° (corr.); *methyl* ester, plates, m. p. 156° (corr.).

In the preparation of 4(or 5)-hydroxymethylglyoxaline by the action of nitric acid on 2-thiol-4(or 5)-aminomethylglyoxaline (T., 1911, **99**, 673), 4(or 5)[*glyoxaline*-4(or 5)-*methyl*]-*glyoxaline*-5(or 4)-*methyl alcohol*, $CH\left\langle\begin{matrix}N\text{—}C\text{——}CH_2\text{——}C\cdot NH \\ NH\cdot CH \qquad OH\cdot CH_2\cdot C\text{—}N\end{matrix}\right\rangle CH$, colourless, silky needles, with $2H_2O$, m. p. 174° (corr.), was obtained as a by-product; *hydrochloride*, prisms, m. p. 178—179° (corr.); *hydrogen oxalate*, with $1H_2O$, m. p. 165° (corr.), with effervescence; *picrate*, long, broad needles, m. p. 197—198° (corr.); *benzoate*, crystals with $1H_2O$ from water, m. p. 67—68° (corr.), nodular aggregates from ethyl acetate, m. p. 120—121° (corr.). D. F. T.

Preparation of Benziminazoles Containing an Ethylamino-group. D. MARON (Eng. Pat., 1915, 1752; (from *J. Soc. Chem. Ind.*, 1916, **35**, 197).—Ethylaminobenziminazoles possessing the property of increasing the blood pressure are obtained from *p*-nitrophenylethylacylamines, $NO_2\cdot C_6H_4\cdot C_2H_4\cdot NH\cdot COR$, by reducing to the corresponding amino-compound, acylating the amino-group, nitrating the acylated product to introduce a nitro-group in the ortho-position to the acylamino-group, and either reducing these nitro-compounds in presence of mineral acids or reducing to the amine, eliminating water, and hydrolysing. Details of the preparation of 5-*ethylamino*-2-*methylbenziminazole*, m. p. 299—300°, and of 2-p-*aminophenyl*-5-*ethylaminobenziminazole* are given. G. F. M.

A Product Obtained in the Manufacture of Natural Indigo. ARTHUR GEORGE PERKIN (T., 1916, **109**, 210—215).—The author has examined three samples of "seeth water," the liquid from which the indigo has settled out at the conclusion of the oxidation process. The solid residues obtained by evaporation of the aqueous liquors consisted of brown, hygroscopic, resinous lumps, the odour of which recalled that of decaying cheese. The solid yielded in each case rather more than 25% of ash, and when acidified the aqueous solutions emitted a strong odour of aliphatic acids, amongst which

acetic and butyric acids were recognisable. Other constituents detected as being present in the resinous mass included an indefinite mixture of nitrogenous, brown substances closely resembling indoxyl-brown (Perkin, T., 1908, **95**, 803), an almost colourless, friable mass, very like indigo-gluten, succinic acid, and a little indigotin.

Stereochemistry of Hydrazones of Alkyl Dithiocarbonates. I. M. Busch (*J. pr. Chem.*, 1916, [ii], **93**, 25—72).—By the nature of the triazolone compound producible with simultaneous scission of a mercaptan from the diphenylsemicarbazone derivative of the isomeric phenylhydrazones of the methyl ethyl and *p*-nitrobenzyl methyl esters respectively of dithiocarbonic acid, the author has been able to demonstrate that the isomerism is of a stereochemical nature (A., 1912, i, 221). The investigation is now extended to other diphenylsemicarbazones of the same type, and in most cases the existence of isomerides is found to be possible, although the two forms are sometimes very easily interconvertible. It was hoped that by replacing one of the alkyl radicles by a methylene or ethylene group, two >C:N-groupings might be included in one molecule, and that, in consequence, three isomeric forms of such a substance might be obtained, but the experimental difficulties proved insuperable. The benzoylhydrazones of the type $NHBz{\cdot}N{:}C{<}^{SR'}_{SR''}$ were also found to be capable of existing in isomeric forms, but these compounds proved to be fairly stable towards alkali, and were not convertible into a diazolone ring-compound, possibly on account of an inability of the compounds to pass into the enolic structure $OH{\cdot}CPh{:}N{\cdot}N{:}C(SR'){\cdot}SR''$. The discovery of the potassium salt and esters of carbazinic acid, $NH_2{\cdot}NH{\cdot}CS_2H$, in this investigation proved of considerable value, because by condensing the esters with an aldehyde, alkylidene compounds of the structure

$$CHR{:}N{\cdot}NH{\cdot}CS_2R'$$

were obtainable, which on alkylation could be converted into substances of the general structure $CHR{:}N{\cdot}N{:}C(SR'){\cdot}SR''$. In the constitution of these compounds the grouping >C:N· is twice included, so that with an unsymmetrical molecule there is a possibility of four stereoisomerides, and this number of isomerides was obtained in the case of the benzylidenehydrazone of methyl *p*-nitrobenzyl dithiocarbonate, $CHPh{:}N{\cdot}N{:}C(SMe){\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$.

[With Wilh. Cornelius.]—When the diphenylsemicarbazone of methyl dithiocarbonate, $NHPh{\cdot}CO{\cdot}NPh{\cdot}NH{\cdot}CS_2Me$, is treated in alcoholic solution with an equimolecular quantity of potassium hydroxide solution and benzyl chloride, the chief product is the *diphenylsemicarbazone* of *methyl benzyl dithiocarbonate*, needles, m. p. 115—116°, accompanied by an isomeride (see below). In the light of the earlier investigation (*loc. cit.*) it is probable that in the main product the benzyl radicle has assumed an *anti*-position with reference to the remainder of the molecule, so that its structure is probably represented by the

formula $\begin{array}{l}NHPh\cdot CO\cdot NPh\cdot N \\ \qquad\qquad\qquad\ \ \| \\ \qquad\qquad SMe\cdot C\cdot S\cdot CH_2Ph\end{array}$, which receives confirmation by the formation of a mercaptan and 3-*benzylthiol*-1 : 4-*diphenyl*-1 : 2 : 4-*triazole*-5-*one*, $\begin{array}{l}NPh—N \\ | \\ CO\cdot NPh\end{array}\!\!>C\cdot S\cdot CH_2Ph$, silky needles, m. p. 112°, under the action of potassium hydroxide; the identity of this substance was confirmed by an independent synthesis from thioldiphenyltriazolone and benzyl chloride in the presence of potassium hydroxide. If the diphenylsemicarbazone of benzyl dithiocarbonate, $NHPh\cdot CO\cdot NPh\cdot NH\cdot CS_2\cdot CH_2Ph$, is allowed to react with methyl iodide in aqueous-alcoholic alkaline solution, the product is a mixture in which the above form of the methyl benzyl ester, m. p. 115—116°, predominates, but in the absence of water at the ordinary temperature the main product is the *isomeride*, $\begin{array}{l}NHPh\cdot CO\cdot NPh\cdot N \\ \qquad\qquad\qquad\ \ \| \\ \qquad CH_2Ph\cdot S\cdot C\cdot SMe\end{array}$, tablets or compact needles, m. p. 127°, which, when treated with alcoholic potassium hydroxide, yields a mercaptan and 3-methylthiol-1 : 4-diphenyltriazolone,

$$\begin{array}{l}NPh—N \\ | \\ CO\cdot NPh\end{array}\!\!>C\cdot SMe.$$

In the interaction of *p*-nitrobenzyl chloride and the diphenylsemicarbazone of benzyl dithiocarbonate in alcoholic solution containing the calculated quantity of potassium hydroxide at the ordinary temperature, the product consisted of a mixture of two isomerides of the *diphenylsemicarbazone* of *benzyl* p-*nitrobenzyl dithiocarbonate*, $\begin{array}{l}NHPh\cdot CO\cdot NPh\cdot N \\ \qquad\qquad\qquad\ \ \| \\ CH_2Ph\cdot S\cdot C\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2\end{array}$, almost colourless needles, m. p. 122—123° (or with benzene of crystallisation, m. p. 105—106°), and $\begin{array}{l}\qquad\qquad NHPh\cdot CO\cdot NPh\cdot N \\ \qquad\qquad\qquad\qquad\qquad\ \ \| \\ NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot C\cdot S\cdot CH_2Ph\end{array}$, colourless needles, m. p. 128°. The author suggests distinguishing these and other isomerides of the same type by naming first the alkyl radicle which stands in a *syn.*-position with respect to the molecule; with this terminology the former compound would be described as the diphenylsemicarbazone of benzyl *p*-nitrobenzyl dithiocarbonate, whilst the latter compound would be termed the diphenylsemicarbazone of *p*-nitrobenzyl benzyl dithiocarbonate. These two compounds behave in the normal way when heated for a short time with potassium hydroxide solution, yielding respectively 3-*p*-nitrobenzylthiol-1 : 4-diphenyltriazolone (Busch, *loc. cit.*) and the above-described 3-benzylthiol-1 : 4-diphenyltriazolone.

In the condensation of *p*-nitrobenzyl chloride and the diphenylsemicarbazone of ethyl dithiocarbonate, the only form of the resulting *diphenylsemicarbazone* of p-*nitrobenzyl ethyl dithiocarbonate* was that represented by the structure

$$\begin{array}{l}NHPh\cdot CO\cdot NPh\cdot N \\ \qquad\qquad\qquad\ \ \| \\ \qquad\qquad SEt\cdot C\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2;\end{array}$$

this substance crystallised in tetragonal prisms, m. p. 142°, and gave 3-*p*-nitrobenzylthiol-1 : 4-diphenyltriazolone when treated with

alkali. Ethylation of the diphenylsemicarbazone of *p*-nitrobenzyl dithiocarbonate gave almost exclusively the same product, a very small quantity of a *substance*, needles, m. p. 111—112°, being formed simultaneously.

The diphenylsemicarbazone of methyl dithiocarbonate was converted by *o*-nitrobenzyl chloride into *o-nitrobenzyl methyl dithiocarbonate diphenylsemicarbazone*,

$$\begin{array}{l} NHPh{\cdot}CO{\cdot}NPh{\cdot}N \\ \qquad\qquad\qquad\quad \| \\ \qquad\qquad SMe{\cdot}C{\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2 \end{array},$$

colourless prisms, m. p. 126°, which on treatment with alkali yielded 3-o-*nitrobenzylthiol*-1 : 4-*diphenyltriazolone*,

$$\begin{array}{l} NPh{-}N \\ | \\ CO{\cdot}NPh \end{array}\!\!>C{\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2,$$

pale yellow needles, m. p. 150—151°; this substance was also prepared by the action of *o*-nitrobenzyl chloride on the potassium salt of 3-thiol-1 : 4-diphenyltriazolone. For the purpose of obtaining the corresponding isomeride, o-*nitrobenzyl dithiocarbonate diphenylsemicarbazone*, $NHPh{\cdot}CO{\cdot}NPh{\cdot}NH{\cdot}CS_2{\cdot}C_6H_4{\cdot}NO_2$, pale yellow needles, m. p. 155—156° (*potassium* derivative, stable), was prepared by the action of phenylcarbimide on *o*-nitrobenzyl phenyldithiocarbazinate, and was then submitted to methylation, but the product was identical with that yielded by the previous process, forming crystals, m. p. 126°, or, with benzene of crystallisation, m. p. 116—117°.

The two isomeric forms of o-*nitrobenzyl* p-*nitrobenzyl dithiocarbonate diphenylsemicarbazone*,

$$\begin{array}{l} \qquad NHPh{\cdot}CO{\cdot}NPh{\cdot}N \\ \qquad\qquad\qquad\qquad\quad \| \\ NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}C{\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2 \end{array},$$

pale yellow leaflets, m. p. 151°, and pale yellow needles, m. p. 147—148°, were respectively obtained by the action of *p*-nitrobenzyl chloride on *o*-nitrobenzyl dithiocarbonate diphenylsemicarbazone and of *o*-nitrobenzyl chloride on *p*-nitrobenzyl dithiocarbonate diphenylsemicarbazone. The *syn.*-*o*-nitrobenzyl compound under the influence of cold alcoholic potassium hydroxide, underwent condensation to 3-*p*-nitrobenzylthiol-1 : 4-diphenyltriazolone, whilst the *syn.*-*p*-nitrobenzyl isomeride in warm alcoholic pyridine solution containing potassium hydroxide gave 3-*o*-nitrobenzylthiol-1 : 4-diphenyltriazolone.

Picryl methyl dithiocarbonate diphenylsemicarbazone,

$$\begin{array}{l} NHPh{\cdot}CO{\cdot}NPh{\cdot}N \\ \qquad\qquad\qquad\quad \| \\ \qquad\qquad SMe{\cdot}C{\cdot}S{\cdot}C_6H_2(NO_2)_3 \end{array},$$

obtained by the interaction of picryl chloride and methyl dithiocarbonate diphenylsemicarbazone, forms orange-red to ochre-coloured prisms, m. p. 154° (decomp.); when the alcoholic solution of this substance is boiled for some time, isomerisation appears to occur, because in addition to the original substance the solution also yields a small quantity of yellow, hexagonal tablets, m. p. 186—187° (decomp.). These crystals are probably of the isomeric form of the preceding substance, but unfortunately an independent

synthesis of this form was impossible on account of the difficulty of producing the necessary *picryl carbazinate*,

$$NHPh \cdot NH \cdot CS_2 \cdot C_6H_2(NO_2)_3,$$

in a pure condition, only an amorphous, brownish-red mass being obtained.

Methylene dithiocarbonate diphenylsemicarbazone,

$$(NHPh \cdot CO \cdot NPh \cdot NH \cdot CS_2)_2CH_2,$$

prepared by the action of phenylcarbimide on methylene phenyldithiocarbazinate at 115—120°, forms colourless needles, m. p. indistinct, near 167° (decomp.). This substance proved resistant to methylation, and an attempt to produce the desired compound or compounds by the action of methylene iodide on an alkaline solution of methyl dithiocarbonate diphenylsemicarbazone failed on account of the reaction going too far even at the ordinary temperature, and yielding 3-*methylenedithioldi*-1 : 4-*diphenyltriazolone*, $CH_2\left(\cdot S \cdot C \begin{array}{l} \lessdot N—NPh \\ \lessdot NPh \cdot CO \end{array}\right)_2$, colourless prisms, m. p. 215°, the identity of which was confirmed by synthesis from methylene iodide and thioldiphenyltriazolone. In the hope of achieving a better result, attention was then turned to the corresponding ethylene derivatives, but with even less satisfaction. Methyl dithiocarbonate diphenylsemicarbazone failed to enter into reaction with ethylene bromide, and the product of the interaction of ethylene bromide and potassium phenyldithiocarbazinate was the undesired cyclic compound, $NHPh \cdot N{:}C \begin{array}{l} \lessdot S \cdot CH_2 \\ \lessdot S \cdot CH_2 \end{array}$. Ethylene di(methyl dithiocarbonate phenylhydrazone), $C_2H_4[S \cdot C(SMe){:}N \cdot NHPh]_2$ (Busch and Lingenbrink, A., 1902, i, 573), proved inactive towards phenylcarbimide, but itself gave indications of isomerisation when kept molten for an hour, giving, on subsequent crystallisation, a mixture of very pale green prisms and stout tablets, the m. p. of the substance having fallen from 108° to 80—85°.

By treating methyl dithiocarbonate diphenylsemicarbazone in cold alcoholic solution with ethyl chloroacetate and an equimolecular proportion of potassium hydroxide, *methyl carbethoxymethyl dithiocarbonate diphenylsemicarbazone*,

$$\begin{array}{r} NHPh \cdot CO \cdot NPh \cdot N \\ \| \\ SMe \cdot C \cdot S \cdot CH_2 \cdot CO_2Et \end{array},$$

colourless prisms, m. p. 97°, was obtained, together with a smaller quantity of the *isomeride*, $\begin{array}{r} NHPh \cdot CO \cdot NPh \cdot N \\ \| \\ CO_2Et \cdot CH_2 \cdot S \cdot C \cdot SMe \end{array}$, needles, m. p. 112°. The former modification, when warmed with potassium hydroxide solution, yielded methyl mercaptan and 1 : 4-*diphenyltriazolonyl*-3-*thiolacetic acid*, $\begin{array}{l} NPh—N \\ | \\ CO \cdot NPh \end{array} \!\!> C \cdot S \cdot CH_2 \cdot CO_2H$, m. p. 175°, which was also prepared independently by the synthesis of the *ethyl* ester, colourless, silky needles, m. p. 84°, from thioldiphenyltriazolone and ethyl chloroacetate. The other isomeride, m. p. 112°, was obtained also by preparing carbethoxymethyl phenyldi-

thiocarbazinate, $NHPh\cdot NH\cdot CS_2\cdot CH_2\cdot CO_2Et$, from potassium phenyldithiocarbazinate and ethyl chloroacetate, and converting this product, by the action of phenylcarbimide, into *carbethoxymethyl dithiocarbonate diphenylsemicarbazone*,

$$NHPh\cdot CO\cdot NPh\cdot NH\cdot CS_2\cdot CH_2\cdot CO_2Et,$$

small, colourless prisms, m. p. 151—152°, which, on methylation, yielded *methyl carbethoxymethyl dithiocarbonate diphenylsemicarbazone*, m. p. 112°. This modification, when treated with alcoholic potassium hydroxide, gives methylthioldiphenyltriazolone, m. p. 101°.

[With MARTIN STARKE.]—*Potassium benzoyldithiocarbazinate*, $NHBz\cdot NH\cdot CS_2K$, needles, can be obtained by the interaction of carbon disulphide, potassium hydroxide, and benzoylhydrazide (m. p. 116·5°; Curtius and Struve, A., 1895, i, 34, give 112·5°) in alcoholic solution, but if an alkyl haloid is added immediately to the solution the product is the corresponding ester. In this way, or by the interaction of the alkyl haloid with the isolated potassium salt, there were prepared the *methyl* ester (colourless needles, m. p. 170°), *ethyl* ester (colourless needles, m. p. 104°), *benzoyl* ester (needles, m. p. 151°), and p-*nitrobenzyl* ester (needles, m. p. 179°); in the preparation of the last two, *dibenzyl dithiocarbonate benzoylhydrazone*, $NHBz\cdot N{:}C(S\cdot CH_2Ph)_2$, pale yellow needles, m. p. 114°, and *di*-p-*nitrobenzyl dithiocarbonate benzoylhydrazone*,

$$NHBz\cdot N{:}C(S\cdot CH_2\cdot C_6H_4\cdot NO_2)_2,$$

colourless prisms, m. p. 157°, were respectively obtained as by-products. All the above esters of benzoyldithiocarbazinic acid possess decided acidic properties and are soluble in aqueous sodium carbonate solution.

By converting an ester of benzoyldithiocarbazinic acid into the corresponding potassium salt, $NHBz\cdot N{:}C(SR)\cdot SK$, by the addition of an equivalent quantity of alcoholic potassium hydroxide and then treating with the calculated quantity of an alkyl haloid at the ordinary temperature, it is possible to obtain "mixed" esters of dithiocarbonic acid benzoylhydrazone. The new compounds are feebly acidic, colourless to pale yellow substances, which are capable of existence in stereoisomeric forms.

Methyl ethyl dithiocarbonate benzoylhydrazone, $\begin{matrix} NHBz\cdot N \\ \| \\ SMe\cdot C\cdot SEt \end{matrix}$, needles, m. p. 46—47°, was obtained by the interaction of methyl benzoyldithiocarbazinate and ethyl iodide, whilst the corresponding *isomeride*, $\begin{matrix} NHBz\cdot N \\ \| \\ SEt\cdot C\cdot SMe \end{matrix}$, obtained from ethyl benzoyldithiocarbazinate and methyl iodide, was a pale yellow oil.

Methyl benzoyldithiocarbazinate and benzyl chloride gave rise to *benzyl methyl dithiocarbonate benzoylhydrazone*,

$$\begin{matrix} NHBz\cdot N \\ \| \\ SMe\cdot C\cdot S\cdot CH_2Ph \end{matrix},$$

needles, m. p. 69°, whilst the isomeride, $\begin{matrix} NHBz\cdot N \\ \| \\ CH_2Ph\cdot S\cdot C\cdot SMe \end{matrix}$, from benzyl benzoyldithiocarbazinate and methyl chloride, formed

needles or leaflets, m. p. 104°; when melted, each of these substances appears to yield an equilibrium mixture of the two isomerides.

p-*Nitrobenzyl methyl dithiocarbonate benzoylhydrazone*,

$$\begin{array}{l} NHBz{\cdot}N \\ \quad\;\, \| \\ SMe{\cdot}C{\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2 \end{array},$$

prepared from methyl benzoyldithiocarbazinate and *p*-nitrobenzyl chloride, forms almost colourless needles, m. p. 117—118°, whilst the corresponding isomeride, $\begin{array}{l} \qquad\qquad\qquad\quad NHBz{\cdot}N \\ \qquad\qquad\qquad\qquad\quad\;\, \| \\ NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}C{\cdot}SMe \end{array}$, from *p*-nitrobenzyl benzoyldithiocarbazinate and methyl iodide, forms colourless needles, m. p. 141°. Partial isomerisation occurs if these compounds are heated above their m. p.'s.

In an endeavour to obtain an ester of dithiocarbonic acid carbomethoxyhydrazone, $CO_2Me{\cdot}NH{\cdot}N{:}C(SR'){\cdot}SR''$, *potassium carbomethoxydithiocarbamate*, $CO_2Me{\cdot}NH{\cdot}NH{\cdot}CS_2K$, was obtained by the interaction of carbon disulphide, potassium hydroxide, and methyl carbazinate (Diels and Fritsche, A., 1911, i, 957) in alcoholic solution, and was further converted through its *potassium* derivative with methyl iodide in alcoholic solution into *methyl carbomethoxydithiocarbamate*, $CO_2Me{\cdot}NH{\cdot}NH{\cdot}CS_2Me$, a mobile, yellow oil. This substance reacted with the calculated quantity of potassium hydroxide, giving a *potassium* derivative, which on treatment with *p*-nitrobenzyl chloride in alcoholic solution, yielded *methyl* p-*nitrobenzyl dithiocarbonate carbomethoxyhydrazone*,

$$CO_2Me{\cdot}NH{\cdot}N{:}C(SMe){\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2.$$

As this substance was an uncrystallisable oil, the investigation was not pursued further in this direction.

If a mixture of hydrazine hydrate and alcoholic potassium hydroxide is treated in the cold with an alcoholic solution of carbon disulphide, *potassium dithiocarbazinate*, $NH_2{\cdot}NH{\cdot}CS_2K$, is obtained, the amount of the accompanying diammonium salt (Curtius and Heidenreich, A., 1896, i, 143) under these conditions being small; the potassium salt crystallises from alcohol in needles which redden in the air. Esters of dithiocarbazinic acid can be prepared by the action of alkyl haloids on the potassium salt, for which purpose the latter need not be isolated; thus the simplest procedure is to add the haloid to the mixture of hydrazine hydrate, alcoholic potassium hydroxide, and carbon disulphide. The esters possess distinctly basic properties, but on account of the possibility of tautomerisation into the structure $NH_2{\cdot}N{:}C(SH){\cdot}SR$ are capable of producing salts with alkalis. *Methyl dithiocarbazinate*, $NH_2{\cdot}NH{\cdot}CS_2Me$, forms colourless prisms, m. p. 79°; *ethyl* ester, a yellow oil; *benzyl* ester, $NH_2{\cdot}NH{\cdot}CS_2{\cdot}CH_2Ph$, colourless needles, m. p. 125°; p-*nitrobenzyl* ester, $NH_2{\cdot}NH{\cdot}CS_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, pale yellow needles, m. p. 143°.

The esters of dithiocarbazinic acid condense readily with aldehydes in warm alcoholic solution, giving alkylidenedithiocarbazinic esters of the general formula $CHR{:}N{\cdot}NH{\cdot}CS_2R'$; indeed, for the production of these compounds it suffices to mix hydrazine hydrate, potassium hydroxide, and carbon disulphide in cold alcoholic solution and to treat the mixture successively with an alkyl haloid

at the ordinary temperature and with an aldehyde on the water-bath. These alkylidene dithiocarbazinic esters are capable of yielding salts derived from the tautomeric structure

$$CHR{:}N{\cdot}N{:}C(SH){\cdot}SR,$$

but, as with the esters of dithiocarbazinic acid, the salts are stable only in alcoholic solution. *Methyl benzylidenedithiocarbazinate*, $CHPh{:}N{\cdot}NH{\cdot}CS_2Me$, forms very pale yellow needles, m. p. 157·5° (decomp.), which give a colourless solution in cold alcohol or benzene, but a yellow solution if the solvent is hot; *benzyl* ester, $CHPh{:}N{\cdot}NH{\cdot}CS_2{\cdot}CH_2Ph$, colourless needles, m. p. 173·5°; p-*nitrobenzyl* ester, $CHPh{:}N{\cdot}NH{\cdot}CS_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$, colourless needles, m. p. 187—188°. *Methyl anisylidenedithiocarbazinate*,

$$OMe{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NH{\cdot}CS_2Me,$$

forms colourless needles or prisms of the monoclinic system, m. p. 167° (decomp.), which resemble methyl benzylidenedithiocarbazinate in giving a colourless solution in cold benzene or alcohol, but a yellow solution if the solvent is warm; indeed, if crystallisation is effected from xylene solution at high temperatures, yellow crystals can be obtained of the same habit and m. p. as the colourless ones. *Methyl* m-*nitrobenzylidenedithiocarbazinate*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NH{\cdot}CS_2Me,$$

forms lustrous, yellow needles, m. p. 192—193° (decomp.); *potassium* derivative, $C_9H_8O_2N_3S_2K$, golden-yellow needles decomposed by water. *Ethyl* m-*nitrobenzylidenedithiocarbazinate*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NH{\cdot}CS_2Et,$$

yellow needles, m. p. 176° (decomp.); *potassium* derivative, silky, golden, or orange-yellow needles, decomposed by water. *Benzyl* m-*nitrobenzylidenedithiocarbazinate*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}NH{\cdot}CS_2{\cdot}CH_2Ph,$$

yellow needles, m. p. 162—163°; *potassium* derivative, slender, yellow needles. Although the possibility of geometrical isomerism exists for these esters, in no case was a second form isolated.

If an ester of an alkylidenedithiocarbazinic acid is treated in alcoholic solution with an equivalent quantity of an alcoholic solution of potassium hydroxide and an alkyl haloid, a mixed ester of dithiocarbonic acid alkylidenehydrazone can be produced. The products, however, are generally so unstable that it is necessary to avoid any rise in temperature.

When methyl benzylidenedithiocarbazinate is treated with benzyl chloride in the described manner, the product contains tetragonal tablets, m. p. 65°, of *benzyl methyl dithiocarbonate benzylidenehydrazone*, $\begin{matrix}CHPh{:}N{\cdot}N\\ \quad\quad\| \\ SMe{\cdot}C{\cdot}S{\cdot}CH_2Ph\end{matrix}$, accompanied by pale yellow needles of the isomeride, $\begin{matrix}CHPh{:}N{\cdot}N\\ \quad\quad\| \\ CH_2Ph{\cdot}S{\cdot}C{\cdot}SMe\end{matrix}$, m. p. 95—96°, which is the exclusive product from benzyl benzylidenedithiocarbazinate and methyl iodide. The most convenient method for preparing the former isomeride is by keeping the latter compound molten for an hour, allowing the resulting mass to crystallise from a mixture of

chloroform and alcohol, and separating the crystals by hand. *Methyl ethyl dithiocarbonate benzylidenehydrazone* and *methyl ethyl dithiocarbonate anisylidenehydrazone* were obtained as uncrystallisable oils. *Methyl ethyl dithiocarbonate* m-*nitrobenzylidenehydrazone*, $NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}N{:}C(SMe){\cdot}SEt$, whether prepared by methylating ethyl nitrobenzylidenedithiocarbazinate or by ethylating the corresponding methyl ester, formed yellow needles, m. p. 96°, one of the isomerides apparently being too labile to exist unaltered. In the preparation of *benzyl methyl dithiocarbonate* m-*nitrobenzylidenehydrazone*,

$$NO_2{\cdot}C_6H_4{\cdot}CH{:}N{\cdot}N{:}C(SMe){\cdot}S{\cdot}CH_2Ph,$$

a mixture of yellow needles, m. p. 107—108° (predominating), and prisms, m. p. 102—103°, was always obtained, whether the reagents were methyl iodide and benzyl *m*-nitrobenzylidenedithiocarbazinate or benzyl chloride and the methyl ester; judging by analogy with other cases, the isomeride of higher m. p. probably has the *syn.*-benzyl configuration.

The interaction of methyl benzylidenedithiocarbazinate and *p*-nitrobenzyl chloride gives a mixture of p-*nitrobenzyl methyl dithiocarbonate benzylidenehydrazone*,

$$\begin{array}{ccc} \mathrm{N} & \text{———} & \mathrm{N} \\ \| & & \| \\ \mathrm{Ph{\cdot}C{\cdot}H} & & \mathrm{SMe{\cdot}C{\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2}, \end{array}$$

colourless, monoclinic prisms, m. p. 101°, with a smaller quantity of the *isomeride*, $\begin{array}{ccc} \mathrm{N} & \text{———} & \mathrm{N} \\ \| & & \| \\ \mathrm{Ph{\cdot}C{\cdot}H} & & \mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}C{\cdot}SMe} \end{array}$, colourless, rhombic or monoclinic leaflets, m. p. 87°, the latter being the exclusive product from *p*-nitrobenzyl benzylidenedithiocarbonate and methyl iodide. These two compounds are easily interconvertible, and when either is fused or kept in boiling alcoholic solution, a mixture of the two isomerides in almost equal quantities is produced. When either of these isomerides is kept in an alcoholic solution of potassium hydroxide at 60—70° for twenty minutes, two further isomerides are formed, one yielding yellow, rhombic, hexagonal tablets, m. p. 154°, probably of the structure

$$\begin{array}{ccc} \mathrm{N} & \text{———} & \mathrm{N} \\ \| & & \| \\ \mathrm{H{\cdot}C{\cdot}Ph} & & \mathrm{SMe{\cdot}C{\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2}, \end{array}$$

and the other, which is produced to a less extent, giving silky, monoclinic needles, m. p. indistinct at 140°, followed by partial solidification and re-fusion to a yellow liquid at 151—152°; the structure of this isomeride is probably

$$\begin{array}{ccc} \mathrm{N} & \text{———} & \mathrm{N} \\ \| & & \| \\ \mathrm{H{\cdot}C{\cdot}Ph} & & \mathrm{NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}C{\cdot}SMe}, \end{array}$$

and its behaviour when heated is due to its tendency to rearrange into the yellow modification. This change also occurs in hot alcoholic solution, especially readily if a little hydrochloric acid is present; the inverse partial change can be effected by warming the yellow modification with very dilute alcoholic potassium hydroxide solution at 70°. D. F. T.

Comparison of the Sörensen, van Slyke, and Colorimetric Methods for the Estimation of Protein Hydrolysis. VICTOR JOHN HARDING and REGINALD M. MACLEAN (*Proc. Amer. Soc. Biol. Chem.*, 1915, xv.–xvi.; *J. Biol. Chem.*, 1916, **24**).—The results show that the van Slyke and colorimetric methods give identical results, which are higher than those given by the Sörensen method. H. W. B.

The Influence of Electrolytes on the Processes of Imbibition. A. The Action of Single Electrolytes. EMIL LENK (*Biochem. Zeitsch.*, 1916, **73**, 15—57).—The imbibition of water by partly hydrated gelatin plates from salt solutions is a function of the concentration of the salts which, as regards their action on this process, can be divided into two classes. In the first class are those salts, of which sodium chloride and thiocyanate are types, in solutions of which the amount of water imbibed by gelatin increases with the concentration. In the second class of salts, of which sodium sulphate is a type, the optimal conditions for imbibition are in concentrations of medium strength. Sodium acetate has an action intermediate between the two classes. The salts of monobasic acids belong to the first class, and those of polybasic acids to the second. The influence of the Hofmeister series of salts on imbibition was investigated. In concentrated solutions the salts of the first group promote imbibition to a greater extent than those of the second ($SCN > Cl > CH_3CO > SO_4$), but the reverse is the case in dilute solutions.

Parallel experiments on the action of salts on beans and on fish have been carried out by the author. S. B. S.

The Influence of Electrolytes on the Processes of Imbibition. B. The Action of Combined Electrolytes. EMIL LENK (*Biochem. Zeitsch.*, 1916, **73**, 58—106).—The imbibition by gelatin in solutions containing more than one electrolyte differs from that taking place in the presence of single electrolytes. In a solution of two salts, in one of which the imbibition is great and in the other small, the imbibition curve lies generally between the curves of the single electrolytes alone, but there are exceptions to this rule when the concentration of one of the electrolytes is very high. If two salts are present together in such concentrations as to produce each the same amount of imbibition, the imbibition produced by the combination is as high as that which is produced by each single salt. In cases, however, where the concentration of both salts is great, the combined action as regards imbibition is greater than that due to the salts singly.

Investigations on the combined action of salts on beans and fish show that the influences of one salt on another as regards toxicity are various. and the combined action is in some cases more toxic and in others less toxic. In some cases the toxic action of one salt can be completely antagonised by another. Attention is called to the parallelism between the action of salts on the production of imbibition and their toxic action on fish.

The various theories of the salt actions are discussed by the author in some detail. S. B. S.

Diastase Accelerators. E. W. Rockwood (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxix.; *J. Biol. Chem.*, 1916, **24**).—Glycine, hippuric acid, and acetamide accelerate the action of the salivary and pancreatic diastases. Anthranilic acid and urea do not exert a similar action on the diastases. H. W. B.

Amino-aliphatic Acids Containing an Arseno-aryl Group. Les Etablissements Poulenc Frères (Eng. Pats., 1915, 17 and 18; from *J. Soc. Chem. Ind.*, 1916, **35**, 275).—Arseno-aryl derivatives of α-amino-aliphatic acids, such as *p*-arsenophenylglycine, are converted into stable derivatives by treating them with formaldehyde in solution. Stable derivatives are also obtained by replacing the hydrogen of the secondary amino-group by an aliphatic or aromatic acyl group, and details are given of the preparation of acetylarsenophenylglycine. The acyl group is preferably introduced into one of the parent substances rather than into the arseno-compound itself. G. F. M.

Preparation of Nitro-compounds of Phenylstibinic Acids and their Derivatives. Chemische Fabrik von Friedr. Heyden (D.R.-P. 287709; from *J. Soc. Chem. Ind.*, 1916, **35**, 197).—Nitrophenylstibinic acids are obtained by treating phenylstibinic acid or its derivatives or substitution products with nitric acid. m-*Nitrophenylstibinic acid* and m-*nitro*-p-*acetylaminophenylstibinic acid* are described. G. F. M.

Organo-derivatives of Bismuth. Frederick Challenger (T., 1916, **109**, 250—251. Compare T., 1914, **105**, 2210; 1915, **107**, 16).—In view of the recent publications of Grüttner and Wiernik (this vol., i, 92, 96) and of the necessary temporary suspension of the present investigation by the author, the following results are now published.

Bismuth trichloride is readily soluble in ether, and the solution reacts with magnesium and *p*-bromotoluene, yielding tri-*p*-tolylbismuthine; when this substance is mixed with a semimolecular proportion of bismuth trichloride, di-*p*-tolylchlorobismuthine, m. p. 181·5°, is obtained. The interaction of triphenylbismuthine and a semimolecular proportion of bismuth tribromide gives diphenylbromobismuthine, together with a little phenyldibromobismuthine. Diphenylbromobismuthine and magnesium *iso*butyl bromide react, giving triphenylbismuthine, a result which may possibly be explained by the instability of mixed aliphatic–aromatic bismuthines.

When triphenylbismuthine is treated with cold sulphuric acid or in chloroform solution with chlorosulphonic acid, the phenyl groups are eliminated. Triphenylbismuthine dichloride reacts with sulphuric acid, yielding hydrogen chloride and a *substance*, probably $BiPh_3SO_4$, which is converted by ammonium sulphide into

triphenylbismuthine; the dihydroxide or oxide gives crystalline *salts* with picric, tartaric, and acetic acids, the *acetate* having m. p. 148—150°.

Triphenylbismuthine dichloride in chloroform solution reacts with chlorosulphonic acid, giving hydrogen chloride and yellow crystals of a *substance* containing bismuth, sulphur, and chlorine. With sulphuryl chloride, thionyl chloride, and sulphur monochloride, triphenylbismuthine yields triphenylbismuthine dichloride, together with other products. Bismuth bromide and the magnesium derivative of ethyl bromoacetate interact, giving a yellowish-white product insoluble in ether. D. F. T.

Physiological Chemistry.

Units of Reference for Basal Metabolism and their Interrelations. C. R. MOULTON (*J. Biol. Chem.*, 1916, **24**, 299—320. Compare Benedict, A., 1915, i, 475).—The weights of the body, fat-free body, blood and nitrogen of the body, and the surface area of a number of cattle have been estimated, and the following relations established by the author from the data obtained.

The weight of the blood is directly proportional to the total nitrogen of the body. A similar relation exists between the weight of the fat-free body and the total nitrogen or the blood of the body. The relations between the surface area (A), the weight of the fat-free body (W), the total nitrogen (N), and the blood (B) are expressed by the following formulæ: $A = 0\cdot1034W^{\frac{2}{3}}$; $A = N^{\frac{2}{8}}$; $A = 0\cdot8B^{\frac{5}{8}}$, the surface area being expressed in square metres and the weights in kilograms. H. W. B.

Protein Synthesis and Metabolic Diseases. N. W. JANNEY (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxx.–xxxi.; *J. Biol. Chem.*, 1916, **24**).—The sparing action of dextrose on the utilisation of protein in the organism is increased by the additional feeding of minute doses of thyroid tissue. The explanation advanced by the author is that the thyroid gland increases the supply of intermediate substances normally produced from dextrose which are thought to be necessary for the synthesis of living protoplasm. H. W. B.

Is the Dextrose Retained when Sodium Carbonate is Administered to De-pancreatised Dogs, Stored as Glycogen? B. KRAMER and J. MARKER (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxiv.; *J. Biol. Chem.*, 1916, **24**).—Sugar retained when sodium carbonate is administered to de-pancreatised dogs is not recoverable as glycogen from the liver, nor is it detected, during the retention, in the saliva, or, afterwards, in the alimentary canal.
H. W. B.

Cell Penetration by Acids. W. J. CROZIER (*J. Biol. Chem.*, 1916, **24**, 255—279).—The rate of cell penetration by acids has been estimated by immersing pieces of tissue from the edge of the nudibranch, *Chromodoris zebra* Heilprin (which contains an intracellular blue pigment, turning pink in the presence of acids), in solutions of various acids with various concentrations, and noting the times which elapse before the colour changes occur. The rate of penetration depends (i) on the degree of ionisation, (ii) on the constitution of the acid. Different regions of the body have different degrees of permeability, and fatty acids penetrate more readily than mineral acids. Similar results were obtained in experiments in which the intensities of stimulation of the acids on the cells of the worm *Eisenia foetida* were estimated by measuring the rate at which one end of the worm immersed in the acid is withdrawn by the other end of the worm immersed in an adjoining vessel of water. H. W. B.

Rôle Played by Electrolytes in Determining the Permeability of Protoplasm. G. H. A. CLOWES (*Proc. Amer. Soc. Biol. Chem.*, 1915, xiv.–xv.; *J. Biol. Chem.*, 1916, **24**).—The effects of the addition of various electrolytes to aqueous solutions of soap or sodium hydroxide on the rate of dropping when passed through olive oil from a Traube stalagmometer have been studied by the author. Since a soap film is formed at the surface of contact between the oil and the water, the number of drops formed is an index of the resistance of the film or of the readiness with which it is dispersed by the constituents of the aqueous phase. It is found that salts of univalent cations promote dispersion of the soap film, and consequently increase its permeability, whilst those of bivalent and tervalent cations promote aggregation of the soap film, and therefore diminish its permeability. Salts of magnesium and anæsthetics at certain optimum concentrations exert a maximum protective effect on the film, which becomes changed to a destructive effect at higher concentrations, and these concentrations are found to correspond very closely with those which exert similar protective and destructive effects on marine organisms. Further, the dispersing effect of sodium chloride can be antagonised by the addition of magnesium salts.

On the basis of these and similar experiments the author sketches a theory relating to the equilibrium of protoplasmic systems.

H. W. B.

Mass Action in the Activation of Unfertilised Starfish Eggs by Butyric Acid. RALPH S. LILLIE (*J. Biol. Chem.*, 1916, **24**, 233—247).—Unfertilised starfish eggs may be caused to develop into larvæ by a sufficiently prolonged exposure to weak solutions of butyric acid in sea-water or van't Hoff's solution, followed by transference to ordinary sea-water. In order to produce complete activation, the eggs must be exposed to the solution for a certain optimum time, which is a function of the concentration of the acid. Exposures briefer than this optimum cause partial activa-

tion—membrane formation, followed by imperfect cleavage and breakdown; activation may be completed by a second exposure to the same solution. Exposures longer than the optimum injure the eggs and interfere with development.

Activation is a progressive process which, under uniform conditions of temperature and physiological state of the eggs, appears to proceed at an approximately uniform rate. This rate is closely proportional to the concentration of the butyric acid, within a range of $0{\cdot}0005N$ to $0{\cdot}006N$. Apparently, the acid activates the egg by combining chemically with some egg constituent until a certain quantity of a definite reaction product is formed. The time required to produce this critical quantity is, in accordance with the mass action law, inversely proportional to the concentration of the acid. H. W. B.

Rate of Oxidations in Reversed Artificial Parthenogenesis. HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1916, **24**, 281—298).—The rate of consumption of oxygen by sea urchin eggs has been studied after development has been artificially initiated and after the initial development has been arrested by placing the eggs in sodium cyanide or chloral hydrate solutions according to the method devised by Loeb. The rate of oxidations, which increases after initiation of development, returns, after reversal, to approximately the original rate of the untreated eggs. On re-treating the reversed eggs with butyric acid so as to initiate development once more, the oxidations are again increased. The spontaneous disintegration of sea urchin eggs preserved in normal, slightly alkaline sea-water is accompanied by a considerable rise in the rate of oxidations, amounting in some cases to a 300 per cent. increase.
H. W. B.

Adrenaline in Human Fœtal Suprarenal Glands. JULIAN HERMAN LEWIS (*J. Biol. Chem.*, 1916, **24**, 249—254).—The author was unable to detect the presence of adrenaline in human fœtal suprarenal glands by chemical tests. On two occasions, however, a slight constricting influence of the extracts on strips of uterus was observed. H. W. B.

Isolation and Properties of Tethelin, the Growth-controlling Principle of the Anterior Lobe of the Pituitary Gland. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1916, **24**, 409—421).—*Tethelin* is precipitated by ether from an alcoholic extract of the anterior lobe of the pituitary gland of the ox. It is obtained as a white or pale cream-coloured, hygroscopic powder which darkens on heating above 100° without melting. It is soluble in water to the extent of about 5 per cent., forming a slightly acid, brown, turbid solution, possessing a greasy odour. It is also soluble in chloroform and in carbon tetrachloride.

The compound contains $1{\cdot}4\%$ of phosphorus, and nitrogen in the proportion of 4 atoms of nitrogen for every atom of phosphorus, two of the atoms of nitrogen being present in amino-groups and

one in an imino-group, which is converted into an amino-group by hydrolysis with barium hydroxide. Among the products yielded by hydrolysis with barium hydroxide followed by hydrolysis with dilute sulphuric acid is *dl*-inositol.

Besides the xantho-proteic reaction, tethelin yields a typical reaction with Millon's reagent; that is, on the addition of a very small quantity of the reagent to an aqueous solution of tethelin a precipitate appears which turns pink on heating. This colour is discharged by adding an excess of the reagent.

Tethelin gives reactions indicating the presence of an iminazolyl group, but does not possess the characteristic physiological properties of the active substances of the posterior lobe of the pituitary gland, which also contains this group (Aldrich, A., 1915, i, 99).

The effects of tethelin on the growth of white mice resemble in every particular the effects of the administration of the whole anterior lobe of the pituitary gland. H. W. B.

Origin and Estimation of Creatine in Muscle. L. BAUMANN, H. HINES and J. MARKER (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxiii.; *J. Biol. Chem.*, 1916, **24**).—The method previously reported by Baumann (A., 1914, ii, 227) has been shortened.

A solution containing choline and urea when perfused through muscle tissue leads to an increase in the creatine content of the muscle. A similar result is not obtained when solutions of arginine, betaine, methyl carbamidoacetic acid, or sarcosine and urea are employed. H. W. B.

Composition of Adipocere. R. F. RUTTAN and M. J. MARSHALL (*Proc. Amer. Soc. Biol. Chem.*, 1915, xii.–xiii; *J. Biol. Chem.*, 1916, **24**).—Adipocere is composed almost entirely of insoluble fatty acids which have resulted from the slow hydrolysis of animal fats by the prolonged action of water. The proteins disappear and the glycerol, soaps, etc., resulting from the hydrolysis are carried away by the water. In the specimen analysed, the fatty acids and traces of fats, etc., soluble in ether constituted 94·1% of the adipocere, and gave the following constants: D^{100} 0·8436; n^{60} 1·436; m. p. 60—63°; acid number, 201·7; saponification number, 207·0; iodine number, 6·04; acetyl number, 34·75.

Besides palmitic acid, 67·52%, stearic acid, 3·3%, and oleic acid, 5·24%, the adipocere contained the characteristic hydroxy-acids, *i*-hydroxystearic acid, 9·48%, and κ-hydroxystearic acid, 6·32%. The total nitrogen was only 0·1778% and the ash 0·578%. H. W. B.

Caseinogen of Goat's Milk. ALFRED W. BOSWORTH and LUCIUS L. VAN SLYKE (*J. Biol. Chem.*, 1916, **24**, 173—175. Compare A., 1913, i, 659, 660).—Caseinogen of goat's milk combines with bases to form the same series of salts (caseinogenates) as in the case of the caseinogen of cow's milk. The proportions of base, sulphur, and phosphorus in these compounds indicate that the molecular weight of the caseinogen of goat's milk is also 8888, and the valency of the protein molecule in the basic caseinogenates is 8.

H. W. B.

Soluble and Insoluble Compounds of Goat's Milk. ALFRED W. BOSWORTH and LUCIUS L. VAN SLYKE (*J. Biol. Chem.*, 1916, **24**, 177—185).—Goat's milk can be separated into two portions by filtration through a Pasteur-Chamberland filter. The filtrate or soluble portion contains lactose, sodium, potassium, and chlorine. The acidity after treatment with normal potassium oxalate (A., 1914, ii, 821) is considerably greater than that shown by the whole milk after similar treatment, which is accounted for by the assumption of the presence of dicalcium phosphate. The residue or insoluble fraction remaining on the filter tube, when suspended in water and treated with normal potassium oxalate, reacts alkaline to phenolphthalein, indicating the presence of tricalcium phosphate. From these and similar data the percentage composition of goat's milk is tentatively suggested to be as follows: Fat, 3·8; proteins combined with calcium, 3·1; lactose, 4·5; dicalcium phosphate, 0·092; tricalcium phosphate, 0·062; dimagnesium phosphate, 0·068; trimagnesium phosphate, 0·024; monopotassium phosphate, 0·073; potassium citrate, 0·250; potassium chloride, 0·160; calcium chloride, 0·115; sodium chloride, 0·095; water, 87·66. H. W. B.

Comparison of the Composition of Cow's Milk, Goat's Milk and Human Milk. ALFRED W. BOSWORTH and LUCIUS L. VAN SLYKE (*J. Biol. Chem.*, 1916, **24**, 187—189).—The total amount of salts in human milk is about one-third that in cow's milk or goat's milk. The number of different salts appears to be greatest in goat's milk and least in human milk. All three milks contain potassium citrate, whilst cow's milk and human milk also contain sodium citrate. Goat's milk contains most chlorides, and human milk the least. In the former, besides calcium chloride, potassium and sodium chlorides appear to be present. Human milk differs noticeably from both cow's milk and goat's milk in containing only soluble phosphates, namely, monomagnesium and monopotassium phosphates. Cow's milk contains insoluble dicalcium phosphate, whilst goat's milk contains di- and tri-calcium and insoluble magnesium phosphates. H. W. B.

Rate of Excretion of Urea. I. Ambard and Weill's Laws of the Excretion of Urea. THOMAS ADDIS and C. K. WATANABE (*J. Biol. Chem.*, 1916, **24**, 203—220. Compare McLean and Selling, A., 1914, i, 1183).—From the consideration of the results of a large number of estimations of urea in blood and urine, the authors conclude that the rate of urea excretion in man varies under physiological conditions in a manner which cannot be explained by any simple law embracing the concentrations of urea in the blood and urine (compare McLean and Selling, *loc. cit.*). There is a tendency in cases in which the concentration of urea in the urine is constant for the higher concentration of urea in the blood to be accompanied by an increased rate of excretion of urea by the kidney. Similarly, in cases in which the concentration of urea in the blood is the same, an increased rate of excretion of urea sometimes produces a lowering in the

concentration of urea in the urine. This relationship is, however, frequently imperceptible. H. W. B.

A New Reaction of Urine. A. BACH (*Compt. rend.*, 1916, **162**, 353—354).—Nitrates and colouring matters are reduced in animal tissues by the combined action of an enzyme and a co-enzyme, neither of which when used alone has any reducing action (compare A., 1914, i, 215). The enzyme is present in fresh milk, but is not accompanied by its co-enzyme. The author has now shown that normal urine contains appreciable quantities of the co-enzyme, indicating the presence of degradation products of the albumins. To estimate the amount of co-enzyme present in the urine, 15 c.c. of the fresh urine are mixed with 10 c.c. of fresh milk and 1 gram of sodium nitrate, and the mixture left for twenty minutes at 60°. At the end of the reaction 0·5 gram of finely powdered basic lead acetate is added, the mixture shaken, filtered through a dry filter-paper, and the amount of nitrite present in 20 c.c. of the filtrate is estimated colorimetrically, as in water analysis. One c.c. of normal urine in the presence of fresh milk can reduce an amount of nitrate corresponding with 0·00001 to 0·00005 gram of N_2O_3.

Blood serum, collected aseptically, does not reduce nitrates in the presence of milk, but if the serum has undergone bacterial fermentation, even with pure cultures, it gives an intense reaction. W. G.

Production of Hyperglycæmia and Glycosuria by Magnesium Salts. I. S. KLEINER and S. J. MELTZER (*Proc. Amer. Soc. Biol. Chem.*, 1915, xx–xxi; *J. Biol. Chem.*, 1916, **24**).—The intravenous injection of a solution of magnesium sulphate produces hyperglycæmia even when respiration is artificially maintained. The hyperglycæmia is therefore not due to asphyxia (compare Underhill and Closson, A., 1906, ii, 186), but it is produced in some way specifically by the magnesium salt. Injection of sodium sulphate does not lead to hyperglycæmia.

The accompanying glycosuria is comparatively small. In some cases it is entirely absent, and when present never reaches 0·5% of dextrose. The diuresis is also scarcely appreciable. H. W. B.

Theory of Diabetes. VI. Behaviour of *dl*-Glyceraldehyde in the Normal and Diabetic Organism. W. D. SANSUM and R. T. WOODYATT (*J. Biol. Chem.*, 1916, **24**, 327—342).—*dl*-Glyceraldehyde may be ingested by normal animals (rabbits and guinea-pigs) in single doses of 1 to 2 grams per kilo. of body-weight without noticeable symptoms, except diminution of urine. The same applies to subcutaneous doses of 0·3 to 1 gram per kilo. Larger doses produce toxic effects and eventually death of the animal. Glyceraldehyde could not be detected in the urine.

In completely phloridzinised dogs and in human diabetes glyceraldehyde may be practically quantitatively converted into dextrose and eliminated in the urine. H. W. B.

Theory of Diabetes. VII. Intravenous Toleration Limit for *dl*-Glyceraldehyde and the Improbability that it is a Chief Intermediate in Dextrose Katabolism. W. D. SANSUM and R. T. WOODYATT (*J. Biol. Chem.*, 1916, **24**, 343—346).—The normal toleration limit for *dl*-glyceraldehyde when injected into the peripheral venous blood of rabbits lies close to 0·15 gram per kilo. per hour, which is only about one-sixth of that for dextrose. It is evident, therefore, that glyceraldehyde is not an intermediate compound formed during the dehydration and utilisation of dextrose in the animal organism. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Chemical Changes in the Souring of Milk. Lucius L. van Slyke and Alfred W. Bosworth (*J. Biol. Chem.*, 1916, **24**, 191—202).—The following changes occur in milk within sixty hours of its inoculation with a culture containing *B. lactis acidi* and *B. lactis aerogenes*: (i) about 22% of the lactose is changed by the bacteria, 88·5% of the amount changed being converted into lactic acid; (ii) citric acid completely disappears; (iii) the insoluble inorganic constituents of the fresh milk are made soluble by the lactic acid; (iv) calcium caseinogenate is changed into soluble calcium lactate and insoluble protein; (v) lactalbumin, towards the end of the period of incubation, passes more readily through a Pasteur-Chamberland filter, owing either to a change in its composition or to its escape from adsorption by the caseinogen of fresh milk.

The rate and extent of chemical change have been ascertained by inoculating fresh, pasteurised "skim" milk with *B. lactis acidi* and incubating at 32·2°, samples being withdrawn for analysis at intervals during ninety-six hours. The results show that (i) the greater part of the lactose is converted into lactic acid between the tenth and the twenty-fourth hours; (ii) when the amount of lactic acid reaches 0·7% the bacterial activity is much reduced; (iii) the acidity increases most rapidly during the first twenty-four hours; (iv) all the calcium passes into solution within twenty-four hours.

H. W. B.

Does Potassium Play any Part in the Protein Synthesis in Plant Cells? Julius Stoklasa (*Biochem. Zeitsch.*, 1916, **73**, 107—160).—A large number of bacteria were cultivated in media containing nitrate as the source of nitrogen, carbohydrates or the salts of organic acids as a source of carbon, together with the other necessary inorganic salts. The amounts of nitrate and sugars, etc., which disappeared during the growth were estimated, as were also the amounts of ammonia and nitrites formed. The amount of

protein formed by the bacteria and the Hausmann numbers of these proteins were also determined. The influence of the nutrient media on the formation of proteins was thereby ascertained. The conclusion drawn from the experiments is, that the formation of new living matter by bacteria, and the protein synthesis, is dependent on the source of carbon employed (carbohydrate or organic acid) when nitrate serves as a source of nitrogen. The nitrate is reduced to nitrite by the hydrogen in statu nascendi, which is derived from the degradation of the carbohydrate or organic acid by the respiratory ferments. The nitrous acid is reduced further to ammonia, which apparently reacts with products derived from the carbohydrates or organic acids to form amino-acids.

One object of the above investigations was to study the influence of light on protein synthesis, for it would appear that the higher plants can synthesise proteins in the dark when there is a supply of carbon in the form of carbohydrate material, organic acids, etc., either in the reserve material or added, and a supply of nitrogen in the form of nitrate.

The synthesis of proteins by bacteria from carbohydrates, etc., and nitrates is, however, very small when no potassium is present, and it appears that this element plays an important part in the dissimilation processes affecting the carbohydrates, etc.

A series of experiments on higher plants was also carried out with the object of investigating the influence of potassium on protein synthesis.

Sugar-beet was grown in pots in the ordinary way, and fed by nutrient solutions containing the usual inorganic salts; in one series of experiments potassium was present; in the other series the same nutrient solution was employed, with the exception that the potassium salt (nitrate) was replaced by a corresponding amount of sodium salt. It was found that those plants which received the nutrient medium containing potassium were far in advance in development of those which received the nutrient solution without this element. Although the percentage of protein in dried material in leaves and roots did not differ much, there were large differences in the total amounts produced. The plants which had received potassium produced also a much larger amount of sugar. The differences in the two series of experiments became much more marked in the later than in the earlier stages of growth.

A further series of experiments on the growth of sugar-beets was carried out in the absence of carbon dioxide (under bell-jars with alkali hydroxide), and the carbon was supplied by various sugars added to the nutrient solutions of inorganic salts. Two series of experiments were carried out, namely, one in which the nutrient solution contained potassium, and one in which this element was absent. Some of the plants in each series were grown in the light, and the others in the dark.

As a result of numerous experiments, the following conclusions were drawn: In an atmosphere free from carbon dioxide, and in the presence of sunlight, plants can produce proteins both in the presence and absence of potassium when dextrose, lævulose, or

sucrose is added as the source of carbon. This synthesis can also take place when no sugars are added, when sufficient plastic organic material is present as reserve matter in the plant. In the absence of light, however, a similar synthesis of proteins can occur where the source of nitrogen is a nitrate, and the source of carbon a carbohydrate, but protein synthesis only takes place in the presence of a potassium salt.

It is therefore only in the absence of light that the importance of potassium in the process of protein synthesis can be demonstrated, and the author calls attention to other researches, which indicate the part which this element plays in the dissimilation of the carbohydrates. S. B. S.

Influence of Hydrogen Peroxide on Germination. E. Demoussy (*Compt. rend.*, 1916, **162**, 435—438).—Seeds of common garden cress which had been kept seven years did not germinate when partly immersed in distilled water at 27°, but showed a 40% germinative capacity after ten days if the water was replaced by hydrogen peroxide (0·25 vol.). Working at 10—14°, however, at the end of fifteen days the germinative capacity in distilled water was 25% and in the hydrogen peroxide 45%. Similarly, when the seeds were placed in damp sand at 27°, 25% germinated. The action of the hydrogen peroxide is to supply oxygen to the seed and at the same time to check microbe development. In distilled water at 27° the microbes are more active than the seed and secure the oxygen, but at 10—14° the reverse is the case. These results only hold good for aged seeds, as fresh seeds germinate well in distilled water at 27°, whilst showing scarcely any signs of life at 12° in the same time. W. G.

Formation of Glucosides by Means of Plants. II. G. Ciamician and C. Ravenna (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 3—7).—The authors have shown (A., 1910, ii, 234) that the absorption by adult plants of certain aromatic compounds leads to the formation of the corresponding glucosides in the plants. Experiments have now been made to see if a similar action can take place during the germination of seeds. The seeds used were those of maize, wheat, beans, lupins, and vetches, and the compounds saligenin, benzyl alcohol, quinol, catechol, gallic acid, and tannin. The last three compounds show, however, toxic properties, and yield no results worthy of mention. Treatment of germinating maize or beans with a solution of saligenin results in the formation of salicin in the plants. Treatment of germinating beans with dilute benzyl alcohol leads to the formation in the plants of a trace of a compound which yields benzyl alcohol when boiled with hydrochloric acid. Similarly, from quinol, which is toxic to maize, germinating beans form a glucosidic compound, probably arbutin. For the production of glucosides in this way the action of light is unnecessary. The fact that salicin is formed in certain plants which are unable to assimilate it is not in agreement with the supposition that glucosides are reserve food materials. T. H. P.

Relative Oxydase Activity of Different Organs of the Same Plant. HERBERT H. BUNZELL (*J. Biol. Chem.*, 1916, **24**, 103—110).—Different parts of a plant contain as a general rule different quantities of oxydase. Thus, the oxydase activities of the leaves of the tulip tree towards pyrogallol, catechol, and quinol are from two to four times as great as the oxydase activities of the buds towards the same reagents. The roots and leaves of potato plants and of sugar-beets showed a similar behaviour; but a corresponding parallelism between the oxydase activities of the roots and leaves of spinach plants could not be established. H. W. B.

Plant Chemistry. P. Q. KEEGAN (*Chem. News*, 1916, **113**, 85—87).—Analyses of hedge mustard (*Alliaria officinalis*), tufted vetch (*Vicia cracca*), bog bean (*Menyanthes trifoliata*), and poppies (*Papaver rhaeus, P. orientalis*, and *Meconopsis cambrica*).
N. H. J. M.

New Sugar (Mannoketoheptose) from the Avocado. F. B. LA FORGE (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxxv.–xxxvi.; *J. Biol. Chem.*, 1916, **24**).—The sugar occurs free in the pulp of the ripe fruit, and can be extracted with water. The concentrated aqueous extract is treated with alcohol to remove the gums, and the sugar isolated from the filtrate in the form of the *bromophenylhydrazone*, m. p. 178°. Cleavage of the bromophenylhydrazone with benzaldehyde yields the free sugar, which crystallises from dilute alcohol in hexagonal prisms, m. p. 152°, $[\alpha]_D^{20}$ +29·5. The sugar is non-fermentable, and is not oxidised by bromine. The osazone, m. p. 200°, appears to be identical with mannoheptosazone.
H. W. B.

Distribution of Quercimeritrin in the Cotton Plant (Gossypium Herbaceum). ARNO VIEHOEVER, LEWIS H. CHERNOFF, and CARL O. JOHNS (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxxiii.; *J. Biol. Chem.*, 1916, **24**).—Quercimeritrin, which hitherto has been obtained only from the petals of the cotton plant (Perkin, T., 1909, **105**, 2185), has now been isolated from the calyx and the leaves. H. W. B.

Protein of the Jack Bean (Canavalia Ensiformis). CARL O. JOHNS and D. BREESE JONES (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxxiii.; *J. Biol. Chem.*, 1916, **24**).—The globulin extracted from the bean has the following percentage composition: C, 52·36; H, 6·90; N, 16·29; S, 0·40; O, 24·05. H. W. B.

Occurrence of β-*p*-Hydroxyphenylethylamine in Various Mistletoes. ALBERT C. CRAWFORD and WALTER K. WATANABE (*J. Biol. Chem.*, 1916, **24**, 169—172. Compare A., 1914, i, 1190).—European mistletoe (*Viscum album*) does not appear to contain β-*p*-hydroxyphenylethylamine. Several more specimens of American mistletoes (*Phoradendron villosum, P. flavescens, P. bolleanum, P. juniperinum*, and *P. californicum*) have been examined, and of

these some have contained the pressor compound whilst others of the same variety have given no evidence of its presence. It is mentioned that the Indians believe that only the mistletoes grown on certain trees are poisonous, which suggests that the host may be responsible for the production of the poisonous substance found in the parasite. H. W. B.

Cedrin, a Glucoside from the Seeds of Simaba Cedron. ARNO VIEHOEVER, G. A. GEIGER, and CARL O. JOHNS (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxxiii.–xxxiv.; *J. Biol. Chem.*, 1916, **24**).—Cedrin, $C_{21}H_{26}O_8$, the bitter principle of *Simaba cedron*, is extracted from the seeds by 95% alcohol. It crystallises in truncated rhombohedrons, m. p. 265° (decomp.), and on hydrolysis yields a sugar which has not been identified. H. W. B.

Presence of Urease in Soja Beans. J. TEMMINCK GROLL (*Chem. Weekblad.*, 1916, **13**, 254—255).—Mom's statement (this vol., ii, 203) that the action of soja beans is due to bacteria, and not to urease, is not confirmed by the author, who finds that the seeds always contain urease. A. J. W.

Urea Estimation by Means of Urease. G. P. MOM (*Chem. Weekblad.*, 1916, **13**, 255—257).—Polemical. A reply to Groll (compare preceding abstract). A. J. W.

The Urease of Soja Beans. W. C. DE GRAAFF and J. E. VAN DER ZANDE (*Chem. Weekblad*, 1916, **13**, 258—264).—The authors find that soja beans sometimes contain bacteria capable of decomposing urea, but not always. These bacteria are not the cause of the ureolytic action of the beans, and no true urobacillus has been detected. The presence of a urease is proved by the action exerted by the seeds after complete sterilisation. A. J. W.

The Milk-juice of Tabernaemontana Sphaerocarpa. A. J. ULTÉE (*Chem. Weekblad*, 1916, **13**, 183—185).—The milk-juice of *Tabernaemontana sphaerocarpa* contains α-amyrin acetate, associated with α-amyrin and other esters. A. J. W.

Saponin from Yucca Angustifolia. ARNO VIEHOEVER, LEWIS H. CHERNOFF, and CARL O. JOHNS (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxxiv.; *J. Biol. Chem.*, 1916, **24**).—The saponin, $C_{36}H_{56}O_{20}$, has been isolated from the root stock of *Yucca angustifolia*. On hydrolysis, it yields galactose. H. W. B.

Saponin from Yucca Radiosa. CARL O. JOHNS, G. A. GEIGER, and ARNO VIEHOEVER (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxxiv.; *J. Biol. Chem.*, 1916, **24**).—The saponin, $C_{37}H_{58}O_{20}$, has been obtained from the root stem of *Yucca radiosa*. On hydrolysis it yields a sugar which is probably dextrose or mannose. H. W. B.

Distribution in Foods of the So-called Vitamines and their Isolation. M. X. SULLIVAN and CARL VOEGTLIN (*Proc Amer. Soc. Biol. Chem.*, 1915, xvi.–xvii.; *J. Biol. Chem.*, 1916, **24**).—Antineuritic substances are present in wheat bran, in the common

black-eyed cow-pea of the Southern States, and in ox-liver, but not in pork fat. H. W. B.

Relation of Lipoids to Vitamines. M. X. SULLIVAN and CARL VOEGTLIN (*Proc. Amer. Soc. Biol. Chem.*, 1915, xvii.; *J. Biol. Chem.*, 1916, **24**).—On extracting wheat bran with 90—95% alcohol and removing the alcohol in a vacuum at 50°, a brownish-yellow lipoid mass is obtained, which is soluble in chloroform and ether. After hydrolysis with acid, a vitamine fraction possessing strong anti-neuritic properties is obtained. The vitamine is, however, not a constituent of a lipoid, because it is the aqueous layer formed after shaking the original lipoid mass with water and ether, which alone yields on hydrolysis a fraction possessing anti-neuritic properties. Apparently, the anti-neuritic material is either dissolved in, or mixed with, the lipoid or is in easily separable combination with it. H. W. B.

Influence of Age and Treatment with Liquid Air on the Sugar-content of Potatoes. H. I. WATERMAN (*Chem. Weekblad*, 1916, **13**, 122—127).—The starch of potatoes which have been cooled by immersion in liquid air is not converted into sucrose by drying at 40°. A. J. W.

Sugar Beet and Potato Tyrosinase. M. GONNERMANN (*Chem. Zeit.*, 1916, **40**, 127—128).—Tyrosinase from potatoes agglutinates blood corpuscles, and when boiled with dilute acids the solution remains clear, indicating the absence of saponin.

Tyrosinase from sugar-beet, on the other hand, is shown by its hæmolysing action on blood to contain saponin. For this reason a solution of sugar-beet tyrosinase shows a feebler reaction with ferrous sulphate and catechol than a solution containing the same amount of tyrosinase from potatoes. N. H. J. M.

Acid Soils and the Effect of Acid Phosphate and other Fertilisers on them. S. D. CONNER (*J. Ind. Eng. Chem.*, 1916, **8**, 35—40).—The various acid constituents of soils exhibit different degrees of acidity with different bases, and even with the same base when free or combined with different acids. The acidity which develops when acid soils are treated with normal salt solutions is probably due to chemical action, and not to selective adsorption; if aluminium silicates are treated with potassium hydroxide solution, heat is developed in the case of hydrogen silicates, but not with normal silicates, indicating a chemical rather than a physical reaction. The acidity of aluminium silicates is in proportion to the ratio of Al_2O_3 to SiO_2, and also to the water of constitution; the greater the proportion of water in the silicate the more acid is the reaction. Heating diminishes the acidity of aluminium hydrogen silicates, the reaction of the compound being neutral when all the water has been expelled; the same effect is noticed when acid soils are ignited. The harmful acidity of soils is due chiefly to the presence of toxic acid salts of aluminium and iron;

the addition of soluble fertiliser salts (nitrates, chlorides, or sulphates) to acid soils increases the quantity of soluble aluminium and iron salts. Soils which have been treated for twenty years with acid phosphate show less acidity than do soils which have not been so treated; acid soils and silicates treated in the laboratory with acid phosphate show less soluble acidity than the untreated soils and silicates. The reduction of soil acidity by acid phosphate is probably due to the action of soluble phosphoric acid on the iron and aluminium salts, non-acid compounds being formed. A method proposed for the estimation of the acidity of soils depends on the hydrolysis of ethyl acetate. The soil is mixed with 5% ethyl acetate solution, and after a definite period, say, eighteen hours, a portion of the solution is titrated with alkali solution; the titration is repeated at definite intervals, and the value of the velocity constant is calculated from the equation $K = I/t \log_e a/a - x$.

W. P. S.

Studies on Soils. I. Basic Exchange. FRANK E. RICE (*J. Physical Chem.*, 1916, **20**, 214—227).—When a soil is shaken with a neutral salt solution, part of the cation of the salt is removed by the soil and other bases are given up to the solution in exchange. The extracts are generally acid to phenolphthalein, and there is much uncertainty as to whether this acidity is due to adsorption by the soil of excess of base, leaving an equivalent quantity of acid in solution, or to the presence of a hydrolysed salt.

Experiments were carried out in which thirty-three different soil samples of 1 gram were shaken with 100 c.c. of normal potassium nitrate solution, left overnight, and filtered. The filtrates were examined by determination of hydrogen-ion concentration, before and after boiling, by Sörensen's method; titration with $N/50$-NaOH; qualitative determination of bases present; and determination of the lime requirement by the Veitch method. Calcium and magnesium were always found in solution; aluminium in the more acid extracts; manganese sometimes, but iron never. An examination with respect to hydrogen-ion concentration of solutions of nitrates of Ca, Mg, Mn, and Al showed that only the aluminium nitrate solution behaved like the soil extracts in being strongly acid and in showing after boiling an increased acidity, returning slowly to its original value. The conclusion is drawn that the acidity of the extract is due to the presence of a hydrolysed aluminium salt and, from similar considerations, that no excess, either of acid or base, can be present. In rare cases excess acid or base may be found when it is present as such in the soil, but this is never to be attributed to selective adsorption by the soil.

The infertility of acid soils is probably due to the presence of loose combinations of the weaker bases, such as alumina, and not to the presence of true "acid hydrogen." E. H. R.

Organic Chemistry.

Does Acetylene Act on Metals? H. Reckleben and Joh. Scheiber (*Chem. Zeit.*, 1916, **40**, 325. Compare A., 1915, i, 113).—Although pure acetylene is without noticeable action on metallic copper, the latter is attacked by crude acetylene, with the formation, among other substances, of copper acetylide, which renders the deposit feebly explosive. As the copper acetylide is apparently completely protected by a coating of sulphide, acetylene could not be detected by boiling it with hydrochloric acid until, after prolonged treatment, the greater part of the sulphide had gone into solution. G. F. M.

Properties of Certain Chloro-hydrocarbons. Sosale Garalapury Sastry (*J. Soc. Chem. Ind.*, 1916, **35**, 450—452. Compare this vol., ii, 188).—Tetrachloroethane is decomposed to a slight extent on boiling with water, with formation of hydrogen chloride. A similar decomposition occurs with sodium acetate solution, and when concentrated aqueous potassium hydroxide is employed, conversion into trichloroethylene to the extent of about 50% is observed. This change is nearly quantitative when the chlorohydrocarbon is treated with alcoholic potassium hydroxide or with sodium ethoxide, but in these cases the trichloroethylene forms a constant boiling mixture with the alcohol, and is isolated by washing and drying over calcium chloride. Tetrachloroethane reacts violently with solid potassium hydroxide, with formation of dichloroethylene, trichloroethylene, and perchloroethylene, and evolution of a spontaneously inflammable gas, probably chloroacetylene. Pentachloroethane behaves similarly to tetrachloroethane when treated with the above reagents. *s*-Dichloroethylene is not acted on by solid or aqueous alkali hydroxides, but alcoholic potassium hydroxide decomposes it, with formation of chloroacetylene. Trichloroethylene is also relatively stable towards solid and aqueous alkalis. G. F. M.

Rearrangement of *iso*Butyl Bromide into *tert.*-Butyl Bromide. A. Michael, E. Scharf, and K. Voigt (*J. Amer. Chem. Soc.*, 1916, **38**, 653—675).—A large number of observations on the isomerisation of *iso*butyl bromide has again been made, on this occasion great care being taken to obtain a specimen with a high degree of purity (compare A., 1911, i, 250; 1912, i, 822). The best *iso*butyl alcohol was purified through its boric ester and converted into the bromide by reagents of the purity required for atomic weight determinations.

The most remarkable fact is established that really pure *iso*butyl bromide is an unstable substance in the liquid phase, some specimens yielding as much as 81·6% of the tertiary bromide on heating at 142° for three hours. In fact, it should only be distilled under reduced pressure; a pure specimen boiled at 91·1—91·25°/

755·5 mm., whilst sharp and constant boiling points are only obtained with less pure products. The behaviour of such impurities as di*iso*butene, *iso*- and *tert.*-butyl alcohol, as negative catalysts of the transformation, that is, as stabilising agents, is confirmed, but special search was made for accelerators. Jena "Geraete" glass has a much greater positive influence than other varieties, and as zinc is the only exceptional constituent of this glass, it may be the active agent, for zinc bromide in the proportion of 0·0001% doubles the amount of the rearrangement. Mercuric chloride is also a powerful positive catalyst. Air has a feeble, positive effect.

The very pure product also undergoes rearrangement in the gaseous state to a greater extent than hitherto observed. One preparation gave about 2·7% of the *tert.*-bromide after heating for three hours at 100° and 53·5% after half an hour at 184°. At the latter temperature, however, *iso*butyl bromide suffers dissociation to the extent of about 50%, so that the rearrangement may partly be due to this; but below 142°, at any rate, transformation must be intramolecular. Strange to say, the rearrangement in the gaseous condition is not accelerated by any of the catalysts which are so active towards the liquid substance. As an explanation of the greater tendency to rearrangement in the liquid state, it is suggested that the change probably goes on in associated molecules with greater energy-content than the gaseous molecules. J. C. W.

Decomposition of Methyl Alcohol by Heated Copper. C. MANNICH and W. GEILMANN (*Ber.*, 1916, **49**, 585—586).—According to Sabatier and Senderens (A., 1903, i, 453), methyl alcohol is decomposed by hot copper into formaldehyde and hydrogen. On attempting to apply this observation to the detection of methyl alcohol, the authors noticed that the intensity of the formaldehyde reaction does not correspond with the volume of hydrogen evolved. Further investigation has shown that at 240—260° the evolved gas consists of hydrogen with 10—12% of carbon monoxide, corresponding with the decomposition of about one-seventh of the primarily formed formaldehyde. A large proportion of the formaldehyde is polymerised to methyl formate, which is readily isolated in the pure state by fractionating the product of the reaction. H. W.

Mechanical Purification of Alcohol by Paraffin. A. POHL (*Chem. Zentr.*, 1916, i, 44; from *Deut. med. Woch.*, **41**, 1373).—Alcohol containing suspended substances, such as dust, can be purified by adding a drop of paraffin, which will retain the dust. Other liquids lighter than paraffin can be purified in a similar manner. N. H. J. M.

Oxidation of Ethyl Alcohol by means of Potassium Permanganate. WILLIAM LLOYD EVANS and JESSE E. DAY (*J. Amer. Chem. Soc.*, 1916, **38**, 375—381).—The authors are making a systematic study of the oxidation of alcohol and similar compounds by neutral or alkaline permanganate, particularly with a view to

determine the effect of temperature and concentration of alkali on the character and relative amounts of the products formed. The present series of experiments at 50° will be followed by others at 25° and 75°, and the discussion of the results will then be presented. J. C. W.

Preparation of Iododihydroxypropane. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (Eng. Pat., 1915, 8488; from *J. Soc. Chem. Ind.*, 1916, **35**, 489).—*Iododihydroxypropane* is obtained as a viscous oil, which eventually solidifies to form crystals of m. p. 48—49°, by treating α-chlorohydrin with an alkali or alkaline earth iodide, preferably in absence of light. The compound is readily soluble in water and alcohol, and is of therapeutic value as a substitute for potassium iodide and organic iodine compounds. G. F. M.

Partial Acylation of the Polyhydric Alcohols and Sugars. II. EMIL FISCHER and CHARLOTTE RUND (*Ber.*, 1916, **49**, 88—105. Compare A., 1915, i, 118).—An extension to erythritol and dextrose of the earlier method for the conversion of dulcitol and mannitol through the acetone derivatives into partly benzoylated compounds.

Erythritolmonoacetone, $C_4H_8O_4(C_3H_6)$, leaflets, m. p. 75—76°, obtainable by treating inactive erythritol with acetone containing 25% of water and 1% of hydrochloric acid, is convertible by benzoyl chloride and quinoline into *dibenzoylerythritolacetone*, $C_4H_6O_4Bz_2(C_3H_6)$, crystals, m. p. 70°, which can be hydrolysed with an acetic acid solution of hydrochloric acid, giving *dibenzoylerythritol* as an oily substance quite distinct from the compound described by Einhorn and Holland (A., 1898, i, 577). In a similar manner, *di*-p-*bromobenzoylerythritolacetone*,

$$C_4H_6O_4(C_3H_6)(CO\cdot C_6H_4Br)_2,$$

crystals, m. p. 147—148° (corr.), was obtained and converted by a mixture of acetic acid and aqueous hydrochloric acid into *di*-p-*bromobenzoylerythritol*, which was also an oil. If the hydrolysis of the di-p-bromobenzoylerythritolacetone is effected with an acetic acid solution of hydrogen chloride, the reaction goes further, acetylation occurring, with formation of *di*-p-*bromobenzoyl*-α-*diacetylerythritol*, $C_4H_6O_4Ac_2(CO\cdot C_6H_4Br)_2$, crystals, m. p. 83—86°; an isomeric *di*-p-*bromobenzoyl*-β-*diacetylerythritol*, m. p. 150—152° (corr.), can be obtained by the acylation of crystalline diacetylerythritol (see below) with bromobenzoyl chloride and quinoline at 65°.

Erythritolacetone can also be acetylated by means of acetic anhydride and pyridine at room temperature, the resulting *diacetylerythritolacetone*, $C_4H_6O_4Ac_2(C_3H_6)$, being a mobile, colourless oil, b. p. 115—120°/0·2 mm., the hydrolysis of which with cold $N/2$-hydrochloric acid yields *diacetylerythritol* as a mixture of a syrupy form with a crystalline isomeride, m. p. 89—91°, partial isomerisation evidently occurring during the acetylation or the hydrolysis; it is the crystalline isomeride which yields the di-p-bromobenzoyl derivative described above.

If dextrosediacetone is heated with *p*-bromobenzoyl chloride and quinoline at 70°, p-*bromobenzoyldextrosediacetone*,

$C_6H_7O_6(C_3H_6)_2 \cdot CO \cdot C_6H_4Br$,

is obtained as microscopic prisms, m. p. 79—80°, $[\alpha]_D^{19}$ −49·2° in acetone; this is hydrolysed by hydrochloric acid in acetic acid solution, giving amorphous p-*bromobenzoyldextrose*,

$C_6H_{11}O_6 \cdot CO \cdot C_6H_4Br$,

which shows mutarotation.

By treatment with benzoyl chloride and quinoline, powdered dextrosemonoacetone is converted into *tribenzoyldextroseacetone*, $C_6H_7O_6Bz_3(C_3H_6)$, colourless needles, m. p. 119—120° (decomp.), $[\alpha]_D^{23}$ −91·9°, which on hydrolysis with a mixture of hydrochloric acid and acetic acid yields *tribenzoyldextrose*, $C_6H_9O_6Bz_3$, as a viscous oil; this combines with carbon tetrachloride, giving an additive *compound*, $C_{27}H_{24}O_9,CCl_4$, which sinters above 65°, decomposes above 80°, and in alcoholic solution shows marked mutarotation. Tribenzoyldextrose can easily be reconverted into its parent tribenzoyldextroseacetone; it also yields a *semicarbazone*, and reduces Fehling's solution.

When mannitol is treated with acetone and aqueous hydrochloric acid, the product contains not only mannitoltriacetone, but also *β-mannitoldiacetone*, $C_6H_{10}O_6(C_3H_6)_2$, needles, m. p. 123—124°, which is quite distinct from the α-mannitoldiacetone of Irvine and Paterson (T., 1914, **105**, 908), and exhibits a very feeble lævorotation in aqueous solution.

A more convenient method for the preparation of the acetone derivatives of glucose is now described (compare Fischer, A., 1895, i, 441; Irvine and Scott, T., 1913, **103**, 569). Instead of taking α-glucose, β-glucose (Behrend, A., 1907, i, 481; 1911, i, 14) is treated with excess of acetone and a little hydrochloric acid at the ordinary temperature, when dextrosediacetone is obtained in good yield, m. p. 110—111° (corr.), $[\alpha]_D^{19}$ −18·4°, from which dextrosemonoacetone, m. p. 161—162·5° (corr.), $[\alpha]_D^{22}$ −11·82° (in water), can be produced by partial hydrolysis with very dilute hydrochloric acid at 50°. This marked difference between the behaviour of α- and β-glucose towards acetone appears to indicate that the acetone compounds are derived from β-glucose.

D. F. T.

Partial Acylation of Polyhydric Alcohols and Sugars. III EMIL FISCHER and MAX BERGMANN (*Ber.*, 1916, **49**, 289—303. Compare A., 1915, i, 118).—The application of the acetone compounds of dulcitol and mannitol in the preparation of partly acylated compounds has been extended to the salicylates and anisates, and a complicated series of isomerides has been found in the case of dulcitol.

When dulcitol-α-diacetone is benzoylated in the presence of quinoline, it yields α-dibenzoyldulcitol-α-diacetone, m. p. 185—186°, but a monobenzoate is formed in chloroform solution. Dulcitol-β-diacetone is now found to yield the same compound, m. p.

185—186°, when treated with benzoyl chloride in chloroform, quinoline, or pyridine. The α-diacetone, however, forms an isomeride, *β-dibenzoyldulcitol-α-diacetone,* if benzoylated in pyridine, and this separates in two forms from alcohol, in hair-like needles, m. p. 82—83°, and in many-faced, hard crystals, m. p. 65—70°. This isomeride, if hydrolysed by a solution of hydrochloric acid in hot ethyl acetate, yields α-dibenzoyldulcitol, m. p. 210°, which the α-isomeride forms if hydrolysed in the cold. If the β-compound is hydrolysed in the cold it yields a mixture of lower melting dibenzoyldulcitols (m. p. 174—175°), which change partly into α-dibenzoyldulcitol on warming with the hydrolysing agent.

Both forms of dulcitoldiacetone yield *α-dianisoyldulcitoldiacetone,* $C_6H_8O_6(C_3H_6)_2(CO{\cdot}C_6H_4{\cdot}OMe)_2$, in radiating groups of lanceolate needles, m. p. 146—147° (corr.), when treated with anisoyl chloride and quinoline at 100°, but the α-diacetone forms the isomeric *β-dianisoyldulcitoldiacetone*, microscopic lances, m. p. 116° (corr.), if acylated in pyridine solution. The α-compound is readily hydrolysed in the cold by a 5% solution of hydrogen chloride in glacial acetic acid to *dianisoyldulcitol*, $C_6H_{12}O_6(CO{\cdot}C_6H_4{\cdot}OMe)_2$, rectangular platelets, m. p. 204—205° (corr.). If dulcitol-α-diacetone is acylated in the cold it yields only a mono-ester, which on hydrolysis forms *monoanisoyldulcitol*, centimetre-long, felted, snow-white needles, m. p. 166—167° (corr.).

Dulcitol-β-diacetone also reacts with carbomethoxysalicoyl [o-methylcarbonatobenzoyl] chloride in the presence of quinoline and chloroform to form *di-o-methylcarbonatobenzoyldulcitoldiacetone*, $C_6H_8O_6(C_3H_6)_2(CO{\cdot}C_6H_4{\cdot}O{\cdot}CO_2Me)_2$, microscopic plates or prisms, m. p. 138—140° (corr.). This may be hydrolysed to disalicoyldulcitoldiacetone (not obtained pure) by means of alcoholic ammonia, and then to *disalicoyldulcitol*,

$$C_6H_{12}O_6(CO{\cdot}C_6H_4{\cdot}OH)_2,$$

microscopic needles, m. p. 219° (corr.), by the usual acid hydrolysis.

When mannitol is shaken with two molecular proportions of anisoyl chloride in warm, dry pyridine and chloroform it yields *dianisoylmannitol*, $C_6H_{12}O_6(CO{\cdot}C_6H_4{\cdot}OMe)_2$, in thin, quadratic plates, m. p. 175—176° (corr.). Similarly, it forms a *di-o-acetoxybenzoyl* derivative, $C_6H_{12}O_6(CO{\cdot}C_6H_4{\cdot}OAc)_2$, colourless needles, m. p. 135—136° (corr.), which is easily hydrolysed by alcoholic ammonia to *disalicoylmannitol*, elongated, rectangular platelets, m. p. 182—184° (corr.), accompanied by a little *monosalicoylmannitol*, thin platelets, m. p. 148—149° (corr.).

Mannitolmonoacetone (Irvine and Patterson, T., 1914, **105**, 907) yields *tetra-acetylmannitolmonoacetone*, $C_3H_6{:}C_6H_8O_6Ac_4$, a viscous oil, b. p. 190—200° (bath)/0·3 mm., when treated with acetic anhydride and pyridine.

Dulcitol-α-diacetone has been examined crystallographically by Steinmetz. It forms monoclinic prisms, $a:b:c = 0{\cdot}7661:1:1{\cdot}0410$; $\beta = 93°59'$.

J. C. W.

Preparation of Esters of Trichlorobutyl Alcohol. R. WOLFFENSTEIN (D.R.-P., 289001; from *J. Soc. Chem. Ind.*, 1916, **35**, 437—438).—The trichlorobutyl hydrogen malonate prepared by the usual esterification methods possesses the same analgesic properties as the original alcohol, without its anæsthetic action.

G. F. M.

The Vapour Pressure of Glyceryl Trinitrate (Nitroglycerin). ARTHUR MARSHALL and GORDON PEACE (T., 1916, **109**, 298—302). —According to previous measurements by the air-bubbling method, the vapour pressure of glyceryl trinitrate at 70° was found to be approximately the same as that of mercury at the same temperature. This method has been subjected to criticism, and new experiments have accordingly been made in which the vapour pressure was determined by passing air through a tube containing powdered cordite at temperatures between 20° and 93°. The vapour pressure increases from 0·00025 mm. at 20° to 0·23 mm. at 90°. The rate of increase of pressure with the temperature is much greater than in the case of mercury, which at 18° has a vapour pressure of 0·001 mm. This value was assumed for glyceryl trinitrate in previous calculations (P., 1913, **29**, 157) of the partial pressure of glyceryl trinitrate in acetone solution, and the requisite corrections are now made. The change does not affect the shape of the partial pressure curve.

H. M. D.

Nitrogenous Constituents of Brain Lecithin. J. E. DARRAH and C. G. MACARTHUR (*J. Amer. Chem. Soc.*, 1916, **38**, 922—930). —Lecithin was prepared from sheep brain and ox brain, and a qualitative and quantitative study made of the nitrogenous constituents of the products of hydrolysis of the different specimens. The lecithin used was carefully purified by a series of solutions and reprecipitations, the criteria of purity being (1) the absence of kephalin; (2) no deposition of "white substance" when allowed to remain in ethereal solution. The lecithin was hydrolysed by heating with 3% hydrochloric acid or 1·6—5% potassium hydroxide solution for fifteen to twenty hours under reflux in the absence of air. From the products of hydrolysis aminoethyl alcohol was isolated, and characterised by preparing its picrolonate and aurichloride. For the quantitative study, the lecithin was further purified by emulsification with water, followed by flocculation with dilute hydrochloric acid. It was then hydrolysed with hydrochloric acid, the fatty acids being filtered off, washed three times with dilute hydrochloric acid, and the nitrogen content of the precipitate determined, this being "residue" nitrogen. The filtrate was evaporated to dryness on a water-bath, the residue being taken up with water and made up to 50 c.c. In 10 c.c. of this the total filtrate nitrogen was estimated. In another 10 c.c. amino-nitrogen was estimated in van Slyke's apparatus, this indicating the amount of amincethyl alcohol present. From a third 10 c.c. the choline was precipitated as its platinichloride, and the nitrogen estimated in the precipitate. In a fourth 10 c.c. the ammonia nitrogen was estimated by Denis's method (compare A., 1911, ii,

163), and in the last 10 c.c. amino-acid nitrogen was estimated by Kober's method (compare A., 1913, ii, 990).

Both sheep- and ox-brain lecithins have about the same nitrogen distribution when freshly prepared. Of the total nitrogen, about 15% is residue or unhydrolysed nitrogen, whilst the hydrolysed or soluble nitrogen, which is about 85% of the total, is present about one-half as choline and the other half as aminoethyl alcohol. There is but little amino-acid nitrogen in lecithin, thus differentiating it from kephalin, and the very small, variable amount of ammonia nitrogen present is probably due to contamination from outside sources.

In what form the residue nitrogen is present is not yet known, but it apparently represents a substance having about the same solubilities as lecithin proper, and attached to it by chemical combination or adsorption so firmly that no known method of purifying lecithin removes it. W. G.

Uranyl Formate. ARNO MÜLLER (*Zeitsch. anorg. Chem.*, 1915, **93**, 267—270).—A slightly acid solution of uranyl nitrate is warmed to 80—90° and mixed with hydrogen peroxide. The precipitate is washed and mixed with an excess of formic acid at 90—100°. The reaction is usually incomplete, but may be made complete and instantaneous by the addition of a little platinised asbestos. The solution is then concentrated under reduced pressure, and finally evaporated in a vacuum over potassium hydroxide and sulphuric acid. Greenish-yellow, hard crystals of uranyl formate, $UO_2(HCO_2)_2,H_2O$, are obtained. The crystals lose their water completely at 110°, becoming greyish-green. The salt is readily soluble in methyl alcohol or water. It yields a basic salt, $UO(OH)_3(HCO_2)$, on evaporating the solution under atmospheric pressure. The crystals darken in light. C. H. D.

Lanthanum Acetate and its Hydrolysis. K. A. VESTERBERG (*Zeitsch. anorg. Chem.*, 1916, **94**, 371—376).—The metallic acetates crystallise with $4H_2O$ or less. The number with $4H_2O$ includes the iron group, and also the rare earths. Various statements have been made regarding lanthanum acetate. It is now found to contain $1\frac{1}{2}H_2O$, of which $\frac{1}{2}H_2O$ is lost at 100°. At 18°, 100 grams of water dissolve 20·43 grams of the anhydrous acetate.

The hydrolysis of the acetate has been determined by extracting the neutral solution in water with ether, and titrating the acid in the ether. A $N/5$ solution is hydrolysed to the extent of 0·31%, and a $N/10$ solution to 0·29%. The strength of lanthanum hydroxide as a base is comparable with that of ammonium hydroxide. C. H. D.

Hardening of Fats by the Catalytic Absorption of Hydrogen. G. FRERICHS (*Arch. Pharm.*, 1915, **253**, 512—573).—According to Erdmann (A., 1913, i, 701; 1915, i, 770), the reduction of nickel oxide by means of hydrogen in presence of an oil is arrested at the formation of a suboxide capable of yielding hydrides of nickel oxide, and thus of serving as a carrier of hydrogen to the oil. The author traverses the evidence advanced in support of this

hypothesis. That metallic nickel is formed when nickel oxide or other nickel compound brings about the hardening of a fat is shown (1) by the electrical conductivity of the catalytic mass, and (2) by the formation of nickel carbonyl when the mass is treated with carbon monoxide, even at 30° (compare Meigen and Bartels, A., 1914, i, 482; Normann and Pungs, A., 1915, ii, 159; Siegmund and Suida, A., 1915, ii, 626). The failure of Erdmann and his collaborators to detect metallic nickel by means of the electrical conductivity is due solely to contamination of the mass by nickel salts of fatty acids, etc. The author regards the presence of free metal as indispensable to the hardening of fats. T. H. P.

Aliphatic Tertiary α-Hydroxy-acids. HANS MAEHLMANN (*Chem. Zentr.*, 1915, ii, 1178; from *Arbeit. Pharm. Inst. Univ. Berlin*, 1914, **11**, 107—129).—The following hydroxy-acids were prepared from the corresponding ketones by the intermediate formation of nitriles with ammonia and hydrocyanic acid.

Methylnonylglycollic acid [*β-hydroxyundecane-β-carboxylic acid*], colourless crystals, m. p. 46° (*copper* salt; *lead* salt; *zinc* salt; *anilide*, leaflets, m. p. 72°; p-*toluidide*, leaflets, m. p. 85°). *Methyloctylglycollic acid* [*β-hydroxydecane-β-carboxylic acid*], colourless needles, m. p. 41°, which yields salts similar to those of the preceding acid. *Methylheptylglycollic acid* [*β-hydroxynonane-β-carboxylic acid*], colourless needles, m. p. 38°; the salts resemble those of the first acid; *anilide*, colourless leaflets, m. p. 86°; p-*toluidide*, leaflets, m. p. 101°. *Methylhexylglycollic acid* [*β-hydroxyoctane-β-carboxylic acid*], colourless needles, m. p. 36°; *anilide*, colourless leaflets, m. p. 85°; p-*toluidide*, m. p. 99°. This acid when heated with 50% sulphuric acid underwent the general fission, giving the original ketone and formic acid; on reduction it yielded the original ketone, and also β-methyloctoic acid, $C_6H_{13}\cdot CHMe\cdot CO_2H$; when converted into the *strychnine* salt, m. p. 118°, it was resolvable into its optical components.

The acids were all optically inactive; on oxidation they gave carbon dioxide, water, and the original ketones, but acetylation could not be effected. Distillation was possible without decomposition at the ordinary pressure. D. F. T.

Action of Oxalic Acid on Crystallised Sodium Sulphate. E. KOHN-ABREST (*Ann. Falsif.*, 1916, **9**, 68—69).—If a mixture of oxalic acid and crystallised sodium sulphate is kept in a closed bottle for twenty-four hours, partial liquefaction occurs, and considerable quantities of sodium hydrogen oxalate and sodium hydrogen sulphate are formed. For instance, a mixture of 300 grams of sodium sulphate and 80 grams of oxalic acid yielded a liquid containing 80 grams of sodium hydrogen sulphate, 3·3 grams of sodium hydrogen oxalate, and 105 grams of water, whilst the remaining crystalline magma contained 117 grams of sodium sulphate and sodium hydrogen sulphate and 91·2 grams of sodium hydrogen oxalate. Owing to the relative insolubility of the sodium hydrogen oxalate, this salt may be separated readily from the sodium hydrogen sulphate, etc. W. P. S.

Barium Oxalate. W. Œchsner de Coninck (*Bull. Soc. chim.*, 1916, [iv], **19**, 110—111).—Neutral barium oxalate can be obtained in the form of four different hydrates, namely, the tri-, di-, mono-, and hemi-hydrates. The optimum temperature of reacting solutions for the trihydrate is 8—10°, for the dihydrate 22—25°, and for the monohydrate 15—18°. The mono- and di-hydrates are generally precipitated simultaneously, and thus it is unsatisfactory to estimate oxalic acid as barium oxalate. The hemihydrate is obtained by the action of a boiling solution of oxalic acid on barium carbonate or nitrate.

Barium hydrogen oxalate only exists as the dihydrate, $Ba(HC_2O_4)_2,2H_2O$. W. G.

The Changes Produced by Time in Officinal Magnesium Citrate. E. Léger (*J. Pharm. Chim.*, 1916, [vii], **13**, 209—214).—The author has determined the amount of matter not soluble in two volumes of water at 70° in a number of samples of officinal magnesium citrate, some of which had been kept one year and others sixteen years. The results show (1) that in the preparation of magnesium citrate, using a temperature only as high even as 50°, tends to favour the transformation of the very soluble citrate into the less soluble citrate; (2) this change occurs during the first year, the salt having then attained an equilibrium, which it keeps for several years. The change which occurs is the transformation of some of the heptahydrate into the tridecahydrate, without the formation of any of the monohydrate.

Pure magnesium citrate, prepared by mixing boiling alcoholic solutions of magnesium acetate and citric acid, does not undergo any change with time, being entirely soluble in two volumes of cold water one year after its preparation. W. G.

Formation of Formaldehyde and other Organic Substances from Formic Acid. I. Auto-reduction of Formates. K. A. Hofmann and K. Schumpelt (*Ber.*, 1916, **49**, 303—317).—If, as is generally assumed, the photosynthesis of carbohydrates in plants involves the production of formaldehyde from carbon dioxide and water, the question must be asked, What is the mechanism of this primary process? The direct scission of carbonic acid, thus, $H_2CO_3 = CH_2O + O_2$, seems to be improbable, and the authors incline to the view that water is first broken down under the influence of light into oxygen, which escapes, and hydrogen, which reduces the carbon dioxide, first to formic acid and then to formaldehyde. These reactions should therefore be attempted in the laboratory. Already it has been shown that the reduction of carbon dioxide (or hydrogen carbonates) by gaseous hydrogen may even be of technical possibility (compare Bredig, A., 1914, i, 377), but the subsequent reduction to formaldehyde has not been very promising. Catalysed auto-reduction of formic acid leads almost entirely to the production of carbon monoxide, carbon dioxide, hydrogen, and water, whilst the thermal decomposition of calcium formate proceeds mainly in the direction $Ca(CO_2H)_2 = CaCO_3 + H_2 + CO$. In connexion with some work on the separation of erbium earths,

however, the authors have discovered that most of the rare earth formates yield formaldehyde on heating, and have made many interesting observations on formates in general.

The powdered formates were mixed with an excess of silica and heated at 450—500°, with a current of moist carbon dioxide streaming over the surface in order to neutralise alkaline oxides and to sweep out the products. Any distillates were tested qualitatively, and formaldehyde was estimated by titration with iodine, whilst carbon monoxide and hydrogen were directly estimated in the gases and methane was found by difference. The yield of formaldehyde rose in the order Ni, Fe, Mn, rare earths, Cu, Th, Na, K, U, Zn, Mg, Ca, Ba, Li, but was considerably masked by the production of empyreumatic substances in the case of Zn, Mn, Mg, Ca, Ba, and the alkalis. Nickel formate gave free nickel, CO, H_2, and CH_4; ferrous formate gave ferrous oxide, CO, H_2, CH_4, and a trace of formaldehyde; didymium formate gave CO, H_2, CH_4, and formaldehyde (1·4% of the theoretical); praseodymium and neodymium formates behaved similarly; cerium formate gave a carbonate, CO, H_2, CH_4, and formaldehyde (1·1%); erbium formate gave a pink oxide, CO, H_2, CH_4, and formaldehyde (1·5%); yttrium and lanthanum formates behaved similarly; thorium formate gave CO, H_2, CH_4, and formaldehyde (1·7%), and, like other rare earths, traces of methyl alcohol; copper formate gave the free metal, CO, H_2, CH_4, and formaldehyde (1·7%); manganese formate gave manganous oxide, a little carbon, CO, H_2, CH_4, and formaldehyde (1·6%); uranyl formate gave U_3O_8, CO, H_2, CH_4, and formaldehyde (3·1%), and was, moreover, observed to decompose, yielding formaldehyde, when its aqueous solution was exposed to the light; zinc formate gave the oxide, CO, H_2, CH_4, and formaldehyde (4·3%). Magnesium formate gave the oxide, carbon, CO, H_2, CH_4, and 3·1% of formaldehyde; calcium formate gave the carbonate, carbon, CO, H_2, CH_4, 7·2% of formaldehyde, and much acetone and methyl alcohol; barium formate behaved similarly, giving 15·6% of formaldehyde and much empyreumatic matter; lithium formate gave dense, white fumes and much carbon, furan derivatives, pyruvic acid, methyl alcohol, acetone, CO, H_2, CH_4, and 10·2% of formaldehyde; sodium and potassium formates gave an almost theoretical yield of the gases.

In the case of lithium formate, about 60% of the compound had given organic derivatives. This result is remarkably influenced by mixing the salt with other formates. For example, equal quantities of lithium formate and nickel formate yielded no formaldehyde and gave an almost quantitative amount of the gaseous products. Nickel formate decomposes first, however, leaving finely divided nickel, and this catalyst causes the lithium formate to decompose in quite another way.

These complicated thermal decompositions can be explained if it is accepted that the first step will be the displacement of hydrogen atoms in the molecule, which may lead to four different results. I. Two hydrogen atoms may combine, leaving an oxalate, which

may then give carbon dioxide and the metal or a carbonate and carbon monoxide, thus, MO_2CH HCO_2M. This will occur when the metal has a large atomic volume and/or a great affinity for oxygen, for example, Na, K, Cu, Pb, Ni. II. Hydrogen may wander from one carbon atom to another, and so displace a ·OM group, with the result that a carbonate and formaldehyde (or equal volumes of carbon monoxide and hydrogen) will be formed, thus, MO_2CH MOCHO. This will be most easily accomplished in the case of multivalent metals, for only one oxygen linking will need to move. Most of the above salts illustrate this. III. The production of ring compounds and empyreumatic substances is due to the decomposition of intermediately formed basic glyoxylates. In order to lead to these, a hydrogen atom wanders to a doubly-linked oxygen, and two carbon atoms then unite, thus, MO_2CH OCHOM. This will be promoted when the metal is strongly basic and multivalent, and is illustrated by Li, Ba, Ca, and Mg formates. IV. These decompositions would yield $CO:H_2$ in no greater proportion than 1:1, whereas in the cases of Li, Mg, Ba, and Th formates it is four to ten times as great. The production of extra carbon monoxide would follow the transference of hydrogen to the oxygen atom attached to the metal, thus, OCH OM. The current of carbon dioxide admitted in the experiments would be favourable to such a decomposition in the case of strongly basic oxides, and excessive carbon monoxide was indeed found in the cases of Li, Mg, Ba, rare earths, Na, K, U, Ca, Mn, Fe, Ni, Pb, Zn, Cu, in descending order. From a measure of the $CO:H_2$ ratio, therefore, it is possible to determine approximately to what extent the decomposition follows scheme IV. compared with the other possibilities. Lithium formate decomposes, for example, nearly five times as much in this direction as in the others. J. C. W.

The Wagner-Saytzeff Reaction with Olefinic Aldehydes. C. J. Enklaar (*Ber.*, 1916, **49**, 211—213).—An impure form of $\Delta^{\alpha\epsilon}$-heptadien-δ-ol has already been obtained (A., 1913, i, 330), and the author has now been able to prepare this compound in a pure condition by the action of allyl bromide and zinc wool on crotonaldehyde in ethereal solution under an atmosphere of carbon dioxide.

Pure $\Delta^{\alpha\epsilon}$-heptadien-δ-ol has b. p. 156—156·7°/765 mm. (decomp.), $D_4^{14.8}$ 0·8668, n_D 1·45527. It undergoes atmospheric oxidation when warmed, and when heated with potassium hydrogen sulphate a molecular proportion of water is lost smoothly. The crotonaldehyde used in its preparation had b. p. 102·2—102·5°/762 mm., $D_4^{20.5}$ 0·8477, n_D 1·43620.

Tiglic aldehyde and methylethylacraldehyde also can be made to undergo a similar reaction with production of alcohols.

D. F. T.

Hydroxymethylenebutanone and a New Method of Preparation for Hydroxymethylene Compounds. OTTO DIELS and KONRAD ILBERG (*Ber.*, 1916, **49**, 158—164).—Azibutanone, N_2:CAcMe (Diels and Pflaumer, A., 1915, i, 127), resembles diazomethane in its chemical behaviour and reacts with formaldehyde in aqueous solution, yielding hydroxymethylenebutanone and nitrogen; the same hydroxymethylene compound is more conveniently obtained by Claisen's method by the interaction of methyl ethyl ketone and ethyl formate in ethereal solution in the presence of sodium ethoxide.

Hydroxymethylenebutanone, COMe·CMe:CH·OH, forms volatile, colourless leaflets of a sweet, rancid odour, m. p. 73°, b. p. 145—147° (slight decomp.); it gives a permanganate colour with ferric chloride in aqueous solution, and yields a *copper* salt, deep green prisms, m. p. 157—158°, a *hydrochloride*, $C_5H_8O_2$,HCl, tablets, decomp. near 107°, and reacts with aniline, ammonia, phenylcarbimide, and hydrazine; the first of these reagents produces an *anil*, needles, m. p. 125—126°, whilst with the last there is obtained the 4:5-dimethylpyrazole already described by Wallach and Wienhaus (A., 1904, i, 104).

Condensation of the hydroxymethylenebutanone with benzaldehyde in hydrochloric acid solution yielded the *hydrochloride*, $C_{18}H_{17}OCl$, colourless leaflets, m. p. 158—159°, of a substance, probably dibenzylidenebutanone, whilst the product in hydrobromic acid solution is the corresponding *hydrobromide*, $C_{18}H_{17}OBr$, prisms, m. p. 149—151°. When heated at 140° in a vacuum desiccator over potassium hydroxide, each of these salts is converted into an uncrystallisable, deep yellow syrup, but it is uncertain whether this is the free dibenzylidenebutanone. Of the possible structures,

CHPh:CH·CO·CMe:CHPh and CHPh:CAc·CH:CHPh,

the former is considered more probable for the expected dibenzylidenebutanone.

D. F. T.

The Rôle of Atmospheric Oxygen in the Oxidation of Dextrose with Potassium Permanganate in the Presence of Varying Amounts of Alkali. The Products of Oxidation. EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1916, **38**, 150—161).—During a study of the oxidation of propylene glycol (A., 1912, i, 743) it was noticed that sometimes only 80% of the theoretical amount of permanganate was required for complete oxidation. The extra oxidation was not due to the reduction of the manganese dioxide, however, but to the participation of atmospheric oxygen. A series of oxidations of dextrose in the presence of varying amounts of potassium hydroxide has now been carried out, and these show with precision the proportions of the end-products formed and the extent of the participation of the atmo-

spheric oxygen, be it to oxidise any manganous oxide or in a direct attack on the sugar.

The greatest deficit in the amount of permanganate required, that is, the greatest participation of the air, occurs with a concentration of alkali of about $0 \cdot 1N$. Carbon dioxide and oxalic acid are the sole end-products, and the proportion of the latter rises rapidly from none to a large amount with a small range of increase in alkalinity. The proportion of oxalic acid is not solely a question of the initial concentration of alkali, however, but depends on the maintenance of the alkalinity. This is because only the normal potassium oxalate is stable in the presence of permanganate; the acid and the acid salt cannot persist.

J. C. W.

Preparation of Acetylbromoglucose. EMIL FISCHER (*Ber.*, 1916, **49**, 584—585).—Acetylbromoglucose is most conveniently prepared according to the following process: powdered, crystalline, anhydrous dextrose (200 grams) is heated on the water-bath with anhydrous sodium acetate (100 grams) and acetic anhydride (1 litre). Complete solution should be attained in thirty minutes. The heating is continued for two hours longer, and the product poured into ice-water (4 litres). The crude β-penta-acetylglucose is crushed, filtered, treated with water until free from acetic anhydride, and crystallised from 96% alcohol. It is then sufficiently pure for further operations, the yield being 74%.

For conversion into acetylbromoglucose, the penta-acetate (150 grams) is treated with the commercial solution of hydrogen bromide in glacial acetic acid (300 grams) for two hours at the ordinary temperature; chloroform (600 c.c.) is added, and the mixture poured into ice-water (2 litres). The chloroform layer is separated, the aqueous portion shaken with a further portion of chloroform (150 c.c.), and the united chloroform extracts washed with water (1 litre). After dehydration over calcium chloride, the chloroform solution is greatly concentrated under diminished pressure, and the residue gradually treated with light petroleum, whereon acetylbromoglucose separates in long needles. It is further purified by rapid recrystallisation from amyl alcohol (75 c.c.), washed with light petroleum, and preserved in a vacuum over soda-lime. The pure product can be preserved unchanged for months, whilst the impure substance becomes coloured fairly rapidly and slowly undergoes extensive change. H. W.

The Phosphoric Acid in Starch. JOHN H. NORTHROP and J. M. NELSON (*J. Amer. Chem. Soc.*, 1916, **38**, 472—479).—Samec (A., 1914, i, 930) assumed that the phosphoric acid present in starch was combined with the amylopectin in such a way that it was easily removed by hydrolysis. The present investigation has shown, however, that the phosphoric acid is combined in the starch grains, and that prolonged boiling with 10% hydrochloric acid is necessary in order to remove it completely.

A potato-starch containing $0 \cdot 06\%$ of phosphorus and not more

than 0·1% of nitrogen was examined. When heated at 65° with 10% hydrochloric acid until it gave no precipitate with alcohol, it lost about 3—5% of the total nitrogen, but a compound containing most of the combined phosphorus could be precipitated by adding much alcohol to the barium salt. Sixty kilos. of starch were treated and 300 grams of the barium precipitate obtained. The salt was converted into a solution of the acid and then into the lead salt, which appeared to be constant in composition (30·4% lead, 3·87% phosphorus), and from this the free *acid* was obtained as a very hygroscopic powder, $[\alpha]_D^{22}$ +108·5°, which contained about 5·3% phosphorus and yielded 65% of dextrose on hydrolysis. Apparently it consists of one molecule of maltose combined with one molecule of phosphoric acid and a hexitol. J. C. W.

Crystalline Polysaccharides from Glycogen. HANS PRINGSHEIM and STEFANIE LICHTENSTEIN (*Ber.*, 1916, **49**, 364—369).—The degradation of starch by Schardinger's *Bacillus macerans* has already been investigated and shown to give rise to a new class of cyclic polysaccharides (A., 1912, i, 832; 1913, i, 1156; 1915, i, 382). Glycogen has now been examined in the same way. A 5% solution was sterilised and left with a potato culture of *B. macerans* at 37°, when it was found that fermentation proceeded at a very much slower rate than in the case of starch, but that the crystalline degradation products were the same, namely, dextrin-β (β-hexa-amylose) and dextrin-α (tetra-amylose). The proportions of these products were different in the two fermentations, however; in the case of starch it was dextrin-α to dextrin-β as 6:1, in the case of glycogen 1:3.

That the amount of starch in the added potato had no influence on the experiments was proved in a parallel test with maltose. No amyloses could be detected even by the iodine reaction, which also shows that if these are formed it is not by building up simpler sugars. J. C. W.

Preparation of Esters of Amino-acids. Amino-acid Esters of Acetone-chloroform. R. WOLFFENSTEIN (D.R.-P., 289426; from *J. Soc. Chem. Ind.*, 1916, **35**, 438).—Amino-acid esters of trichlorotrimethylcarbinol (acetone-chloroform) are prepared by the condensation of the monohalogen-acetic esters of that alcohol with secondary aliphatic amines. tert.-*Trichlorobutyl dimethyl-* and *diethyl-aminoacetate* prepared in this way form easily soluble hydrochlorides which have strong soporific properties. G. F. M.

Certain Nitrogenous Derivatives of Pimelic Acid. ERNST SCHMIDT (*Arch. Pharm.*, 1915, **253**, 604—621. Compare this vol., i, 285).—The assumption that the action of methylamine on ethyl αε-dibromopimelate is analogous to that of ammonia and proceeds according to the equation

$$CH_2(CH_2\cdot CHBr\cdot CO_2Et)_2 + 3NH_2Me = CH_2<\begin{matrix}CH_2\cdot CH(CO\cdot NHMe)\\ CH_2\cdot CH(CO\cdot NHMe)\end{matrix}>NMe + 2HBr + 2EtOH,$$

is not confirmed experimentally. The product obtained under the experimental conditions employed, when boiled with barium hydroxide solution, yields principally anhydrodimethylaminopimelic acid, $CO_2H\cdot CH(NHMe)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH<\begin{matrix}NMe\\|\\CO\end{matrix}$

Whether this compound is formed as the methylamide,

$$NHMe\cdot CO\cdot CH(NHMe)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH<\begin{matrix}NMe\\|\\CO\end{matrix},$$

in the reaction or whether it results from the action of the barium hydroxide on the initial dimethylaminopimelomethylamide, $CH_2[CH_2\cdot CH(NHMe)\cdot CO\cdot NHMe]_2$, is not yet established. Attempts were made to convert the initial product of the reaction into the hydrochloride and aurichloride, but these are difficult to purify and have not been obtained pure.

Anhydrodimethylaminopimelic acid, $C_9H_{16}O_3N_2$, forms white, needles, sometimes united to drusy masses, m. p. 195—196° (efferves.). The corresponding *hydrochloride*, m. p. 201—202° (efferves.), *aurichloride*, m. p. 190° (efferves.), *platinichloride*, m. p. 215° (efferves.), and *copper* salt, $(C_9H_{15}O_3N_2)_2Cu,CuO,7H_2O$, were prepared.

Dimethylaminopimelic anhydride, $CH_2\left(CH_2\cdot CH<\begin{matrix}NMe\\|\\CO\end{matrix}\right)_2$, also formed in this reaction, yields a *hydrochloride*, m. p. 224—225°, and an *aurichloride*, m. p. 189—190° (efferves.), which may be converted into the aurichloride described above.

The mother liquor of the reaction products yields also another *aurichloride*, $C_9H_{16}O_3N_2,HAuCl_4$, m. p. 180—182° (efferves.), with previous sintering; under certain conditions this undergoes conversion into the two aurichlorides described above, but the reverse change has not been observed. The corresponding *hydrochloride* has m. p. 190° (efferves.).

The mother liquor yields, further, a copper salt,

$$C_5H_8NMe(CO_2)_2Cu,5H_2O,$$

identical in properties and composition with that of methylpiperidinedicarboxylic acid obtained by cautious oxidation of hydroscopoline (A., 1909, i, 173). Examination of the free acid, its hydrochloride and aurichloride, confirms the identity of the two products, which represent 1-methylpiperidine-2:6-dicarboxylic acid.

Hess and Suchier (this vol., i, 285) are trespassing on the author's field of work. T. H. P.

Synthesis of Polypeptides of High Molecular Weight from Glycine and *l*-Leucine. EMIL ABDERHALDEN and ANDOR FODOR (*Ber.*, 1916, **49**, 561—578).—The investigation was undertaken with the twofold object of preparing polypeptides of high molecular weight and known constitution, which would be suitable for investigation of the action of definite ferments, and of determining the minimum molecular weight at which colloidal properties become manifest. In general, the polypeptides are obtained by the action of *d*-bromo*iso*hexoyldiglycylglycyl chloride on the requisite

glycine derivative, and subsequent treatment of the product with ammonia. Especially with the higher members of the series, considerable difficulties are experienced in the separation of the complex halogen derivative from simultaneously formed bromo*iso*hexoyldiglycylglycine, since, in contrast to the cases investigated by Fischer, they do not directly separate when the solutions are acidified, whilst, further, their solubility in alcohol is considerably increased in the presence of the by-product.

Diglycylglycine, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, is conveniently prepared by the action of chloroacetyl chloride on a solution of glycine anhydride in sodium hydroxide, and subsequent treatment of the chloroacetylglycylglycine with 25% ammonia at 37° for a period of not more than twenty-four hours.

d-*Bromo*iso*hexoylglycylglycine*, shining leaflets, m. p. 130—132°, $[\alpha]_D^{20}$ +47·01° in alcohol, $[\alpha]_D^{20}$ +31·17° in water, $[\alpha]_D^{20}$ +26·24° in *N*/10-sodium hydroxide solution, is obtained by the action of *d*-α-bromo*iso*hexoyl chloride on glycine anhydride in the presence of sodium hydroxide. When treated with 25% ammonia it is converted into l-*leucylglycylglycine*,

$CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$,

$[\alpha]_D^{20}$ +45·90°, in aqueous solution. This substance is very readily soluble in water, and is not salted out by saturated ammonium sulphate solution. It gives a bluish-violet biuret reaction.

d-*Bromo*iso*hexoyltriglycylglycine*, leaflets, m. p. 186—188°, $[\alpha]_D^{20}$ +22·55° in water, $[\alpha]_D^{20}$ +25·47° in *N*/10-sodium hydroxide, is prepared from *d*-bromo*iso*hexoyl chloride and triglycylglycine, and is converted by ammonia into l-*leucyltriglycylglycine*,

$CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH_2\cdot CO_2H$,

colourless powder, $[\alpha]_D^{20}$ +28·14° in water. It is readily soluble in water, from which it is not precipitated by ammonium sulphate. It gives a blue biuret reaction.

Two methods are described for the preparation of d-α-*bromo*iso*hexoylpentaglycylglycine*. In the first of these, diglycylglycine methyl ester hydrochloride is dissolved in methyl alcohol and treated with the requisite quantity of sodium ethoxide solution, whereby pentaglycylglycine methyl ester is obtained, from which, after hydrolysis, pentaglycylglycine is isolated; this, when treated in the usual manner, yields *d*-α-bromo*iso*hexoylglycylglycine, which decomposes at 238—240° and has $[\alpha]_D^{20}$ +18·19° in aqueous solution. In the second method, pure diglycylglycine is treated with *d*-bromo*iso*hexoyl chloride, and the product, after thorough desiccation, is submitted to the action of phosphorus pentachloride in the presence of acetyl chloride; *d*-α-bromo*iso*hexoyldiglycylglycyl chloride is thus obtained, which is converted by treatment with diglycylglycine in the usual manner into *d*-α-bromo*iso*hexoylpentaglycylglycine, $[\alpha]_D^{20}$ +18·33° to +19·49° in *N*/10-sodium hydroxide; it decomposes at 235—240° (uncorr.) after softening at 220°. l-*Leucylpentaglycylglycine*,

$CHMe_2\cdot CH_2\cdot CH(NH_2)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_5\cdot NH\cdot CH_2\cdot CO_2H$

(obtained from the above halogen compound and ammonia), has $[\alpha]_D^{20}$ +5·94° in N/10-sodium hydroxide. It is fairly readily soluble

in water, and is precipitated from its aqueous solution by addition of ammonium sulphate. It gives a reddish-violet biuret reaction.

l-Leucylpentaglycylglycine is transformed in the usual manner into d-*α-bromo*iso*hexoyltriglycyl*-l-*leucylpentaglycylglycine*, microcrystals, decomposing at 230—235°, $[\alpha]_D^{20}$ +7·34° in N/10-sodium hydroxide, which is converted by liquid ammonia into l-*leucyltriglycyl*-l-*leucylpentaglycylglycine*,

$$\begin{array}{l} NH\cdot[CO\cdot CH_2\cdot NH]_3\cdot CO\cdot CH(NH_2)\cdot CH_2\cdot CHMe_2 \\ CH(CH_2\cdot CHMe_2)\cdot CO\cdot[NH\cdot CH_2\cdot CO]_5\cdot NH\cdot CH_2\cdot CO_2H \end{array}$$

This polypeptide is a voluminous white powder which, like the more complex polypeptides, is fairly readily soluble in hot water and does not separate when the aqueous solution is cooled. It is immediately precipitated by addition of ammonium sulphate and gives a reddish-violet biuret reaction. In N/10-sodium hydroxide solution it has $[\alpha]_D^{20}$ −6·00°.

Starting from this polypeptide, and by a similar series of reactions, d-*α-bromo*iso*hexoyltriglycyl*-l-*leucyltriglycyl*-l-*leucylpentaglycylglycine* (indistinct, crystalline mass, which decomposes at 210—230° after darkening at 200°, $[\alpha]_D^{20}$ −4° in N/10-sodium hydroxide) and l-*leucyltriglycyl*-l-*leucyltriglycyl*-l-*leucylpentaglycylglycine* ($[\alpha]_D^{20}$ −9·63° in N/10-sodium hydroxide) are prepared.

By a continuation of the process, d-*α-bromo*iso*hexoyltriglycyl*-l-*leucyltriglycyl*-l-*leucyltriglycyl*-l-*leucylpentaglycylglycine* (voluminous white powder, $[\alpha]_D^{20}$ −8° in N/10-sodium hydroxide), and, finally, l-*leucyltriglycyl*-l-*leucyltriglycyl*-l-*leucyltriglycyl*-l-*leucylpentaglycylglycine*,

$$\begin{array}{ll} CH(NH_2)\cdot CH_2\cdot CHMe_2 & CO_2H\cdot CH_2 \\ CO\{[NH\cdot CH_2\cdot CO]_3\cdot NH\cdot CH(CH_2Pr^{\beta})\cdot CO\}_3\cdot[NH_2\cdot CH_2\cdot CO]_5\cdot NH \end{array}$$

($[\alpha]_D^{20}$ −8·42° in N/10-sodium hydroxide), are prepared. H. W.

Spectrophotometric Study of Copper Complexes and the Biuret Reaction. PHILIP ADOLPH KOBER and ARTHUR B. HAW (*J. Amer. Chem. Soc.*, 1916, **38**, 457—472. Compare A., 1912, i, 952, 953).—In the earlier papers it was laid down that the copper complexes of amino-acids and similar substances could be divided into three classes, according to their outward appearance, and the connexion between the number of nitrogen groups which could link with the copper atoms and the colours of the complexes was established. A large number of these complexes have now been examined in a systematic way by means of the spectroscope, and it is again demonstrated that the blue, purple ("semi-biuret"), and red (biuret) colours represent three, and only three, classes of compounds.

The experiments are described in detail, and in a general discussion it is again pointed out that the results indicate that the red colours of the complexes are due to the presence of nitrogen groups alone. Other features of the problem and replies to criticisms of the earlier papers are reserved for a future communication. J. C. W.

Stability of Silver Fulminate under Water. ALFRED M. PETER (*J. Amer. Chem. Soc.*, 1916, **38**, 486).—A specimen of silver fulminate which had been preserved under water in a well-stoppered bottle for at least thirty-seven years was found to be quite good, being merely a little discoloured by the light.

J. C. W.

Alkylcyanoacetic Acids. JOHN C. HESSLER [with THOMAS B. MAGATH, FRED F. JOEL, and MARGARET C. HESSLER] (*J. Amer. Chem. Soc.*, 1916, **38**, 909—916).—Several new alkylcyanoacetic acids, their salts and derivatives, have been prepared. The dialkylcyanoacetic esters were saponified by potassium hydroxide in methyl alcohol.

α-Cyano-α-methylpropionic acid, $CN\cdot CMe_2\cdot CO_2H$, m. p. 57°, b. p. 132—135°/12 mm., was readily obtained from its ethyl ester by the action of potassium hydroxide in methyl alcohol in the cold. It gave a *silver* salt, $C_5H_6O_2NAg$, long, slender needles, and a *barium* salt, $C_{10}H_{12}O_4N_2Ba,18H_2O$, long prisms.

α-Cyano-α-ethylbutyric acid, m. p. 66° (compare Hesse, A., 1897, i, 18, who found m. p. 57°), gave a *silver* salt, $C_7H_{10}O_2NAg$; a *barium* salt, $C_{14}H_{20}O_4N_2Ba$, slender needles; a *calcium* salt, $C_{14}H_{20}O_4N_2Ca,3H_2O$, long needles; a *strontium* salt,

$$C_{14}H_{20}O_4N_2Sr,3H_2O,$$

long prisms; a *lead* salt, $C_{14}H_{20}O_4N_2Pb$, flaky crystals; a *cadmium* salt, $C_{14}H_{20}O_4N_2Cd,3H_2O$, irregular plates; and a *copper* salt, $C_{14}H_{20}O_4N_2Cu,3H_2O$, rectangular green crystals.

Ethyl cyanoacetate when mixed with propyl iodide in absolute alcohol in the presence of sodium gave a mixture of cyanovaleric and cyanopropylvaleric esters. This mixture was shaken twice in ethereal solution with an excess of 10% aqueous sodium hydroxide. The ether was separated off, and contained the cyanopropylvaleric ester. The aqueous solution was acidified with dilute sulphuric acid and extracted with ether, from which extract *α-cyanovaleric acid*, $CN\cdot CHPr\cdot CO_2H$, was obtained. It gave a *silver* salt, $C_6H_9O_2NAg$; a *barium* salt, $C_{12}H_{18}O_4N_2Ba$; and an *ethyl* ester, b. p. 218—219°/755 mm., D^{32} 0·972. The ethereal solution unattacked by the alkali yielded on distillation *ethyl α-cyano-α-propylvalerate*, b. p. 129—132°/21—23 mm., D^{26} 0·93. The ester, on saponification, yielded the free *acid*, m. p. 41°, giving a *silver* salt, $C_9H_{14}O_2NAg,H_2O$, which lost its water of hydration when dried in a vacuum over sulphuric acid.

Prepared by a similar method were *α-cyano-γ-methylvaleric acid*, $C_4H_9\cdot CH(CN)\cdot CO_2H$, giving a *silver* salt, $C_7H_{10}O_2NAg$; a *barium* salt, $C_{14}H_{20}O_4N_2Ba,2H_2O$; and an *ethyl* ester, b. p. 223—224°/755 mm., D^{35} 0·958. *α-Cyano-γ-methyl-α-*iso*butylvaleric acid*, m. p. 82°, gave a *silver* salt, $C_{11}H_{18}O_2NAg$, and an *ethyl* ester, b. p. 245—250°/755 mm., D^{31} 0·915.

δ-Methylhexoic acid (compare A., 1913, i, 1038) yielded a *copper* salt, $C_{16}H_{24}O_4N_2Cu,7H_2O$; a *barium* salt, $C_{16}H_{24}O_4N_2Ba,2H_2O$, in tufts of white needles; an *acid chloride*, and an *anilide*, m. p. 102°.

Ethyl α-cyano-δ-methyl-α-*iso*amylhexoate (*loc. cit.*), on saponification yielded the free *acid*, white needles, m. p. 74—75°, giving an *ammonium* salt; a *silver* salt, $C_{13}H_{22}O_2NAg$; a *copper* salt, $C_{26}H_{44}O_4N_2Cu,3H_2O$; a *calcium* salt, $C_{26}H_{44}O_4N_2Ca,4H_2O$; and an *amide*, $C_{13}H_{24}ON_2$, needles, m. p. 152°.

α-Cyano-β-phenylpropionic acid, m. p. 101° (compare *J. Amer. Chem. Soc.*, 1899, **22**, 176), gave a *lead* salt, $C_{20}H_{16}O_4N_2Pb,3H_2O$, which lost its water of hydration in a vacuum over sulphuric acid; a *barium* salt, $C_{20}H_{16}O_4N_2Ba,6H_2O$; a *calcium* salt,

$$C_{20}H_{16}O_4N_2Ca,3H_2O,$$

and its anhydrous salt; a *copper* salt, $C_{20}H_{16}O_4N_2Cu,5H_2O$, decomposing at 105—115°; and an *acid chloride*. α-Cyano-β-phenyl-α-benzylpropionic acid gave a *silver* salt, $C_{17}H_{14}O_2NAg$, and a *copper* salt, $C_{34}H_{28}O_4N_2Cu,H_2O$.

Ethyl cyanoacetate when treated with benzyl chloride in methyl alcohol solution in the presence of sodium methoxide yielded a mixture of an ester of cyanophenylpropionic acid and *methyl cyanophenylbenzylpropionate*, hexagonal plates, m. p. 78—79°.

W. G.

The Presence of Benzene Homologues in the High-boiling Distillates of Petroleum. BENJAMIN T. BROOKS and IRWIN W. HUMPHREY (*J. Amer. Chem. Soc.*, 1916, **38**, 393—400).—The fluorescent substances in petroleum distillates are most probably benzenoid, but although it is well known that petroleums contain small amounts of benzene and its simpler homologues, few attempts have been made to isolate the higher members. The authors have therefore submitted some high-boiling oils to "cracking" at temperatures much below the point at which the profound decomposition, which results in the formation of gaseous and benzenoid hydrocarbons, is likely to occur. They find that fractions of certain crude petroleums, with b. p. above 275°, yield benzene, toluene, and *m*-xylene when heated at 420° under a pressure of 100 lb. per square inch or with aluminium chloride at 300°; that pure paraffin-wax does not yield benzenes or fluorescent distillates on cracking under these conditions, but that a synthetic "phenyl-paraffin," made by chlorinating paraffin-wax and then condensing the product with benzene in the presence of aluminium chloride and carbon disulphide, is readily cracked at 420°/100 lb., or by merely heating with aluminium chloride at 230° to give benzene and toluene. The formation of toluene in the last case indicates that the phenyl-paraffin undergoes scission, a reaction that would give another interpretation of the fact that naphthalene is formed when coal is distilled at 350° in a vacuum (Jones and Wheeler, T., 1914, **105**, 2562); thus, $C_{10}H_7\cdot C_nH_{2n+1}$, a naphthyl-paraffin, might yield $C_{10}H_8$ and C_nH_{2n}.

Details of the experiments are given. It may be said that the benzene homologues were extracted from the distillates by shaking with liquid sulphur dioxide, and identified as nitro-compounds.

J. C. W.

Sodium Triphenylmethyl. W. SCHLENK and RUDOLF OCHS (*Ber.*, 1916, **49**, 608—614).—The action of an ethereal solution of

sodium triphenylmethyl on esters, ketones, aldehydes, and certain other substances has been investigated. In general, properties of this reagent are very similar to those of Grignard's reagents, but the actions are complete in a much shorter time. Owing to the tendency of the reagent to exchange its sodium atom for hydrogen, it cannot be used for condensations with acetone, ethyl acetate, and similar substances, which in this case behave as pure enols.

The reagent is conveniently prepared by shaking a solution of triphenylchloromethane in dry ether with sodium amalgam (2%) for one or two days.

Sodium triphenylmethyl and methyl benzoate yield β-benzpinacolin, pale yellow, crystalline powder, m. p. 179°, in accordance with the equation $CPh_3Na + Ph{\cdot}CO_2Me = CPh_3{\cdot}COPh + NaOMe$. Molecular quantities of sodium triphenylmethyl and methyl p-chlorobenzoate give p-*chloro-β-benzpinacolin*, needles, m. p. 168°.

Formaldehyde is readily converted into triphenylethanol, $CPh_3{\cdot}CH_2{\cdot}OH$, colourless needles, m. p. 107° (slight decomp.), which when heated above its m. p. decomposes into triphenylmethane and formaldehyde. Benzaldehyde yields tetraphenylethanol, m. p. 151°, whilst furfuraldehyde gives *triphenylfurylethanol*, needles, m. p. 125°. On the other hand, aldehydes, such as butaldehyde, which can react in an enolic form, give rise to triphenylmethane.

The action of ketones is dissimilar from that observed with Grignard's reagents. Those which can pass into an enolic form cannot be employed, and with diarylketones a condensation is not observed; thus, with benzophenone, pentaphenylethanol is not obtained, but the solution becomes green, owing to the formation of metallic ketyls, according to the scheme $CPh_3Na + COPh_2 \rightleftarrows CPh_3{\cdot}CPh_2{\cdot}ONa$. With distyryl ketone, terastyrylpinacolin, m. p. 167—168°, is produced, but the somewhat analogously constituted phorone behaves as an enol—a fact which leads the authors to doubt the constitution generally assigned to this substance.

Sodium triphenylmethyl and sulphur dioxide yield *sodium triphenylmethylsulphinate*, which contains ether of crystallisation and rapidly decomposes on exposure to air. The aqueous solution when cooled deposits a crystalline *hydrate*. With ammonia, sodium triphenylmethyl yields sodamide and triphenylmethane, but no reaction appears to occur with carbon dioxide. H. W.

Organic Molecular Compounds. JAMES F. NORRIS [with KATHERINE E. ROONEY, JANET S. MURPHY, and CAROLYN F. DODGE] (*J. Amer. Chem. Soc.*, 1916, **38**, 702—711).—The author is engaged in an investigation of the conditions governing the formation of molecular additive compounds, and finds a simple explanation of the phenomena in a restatement of Berzelius's electrochemical theory. Roughly speaking, when elements unite, their inherent energy may not all be transformed in the building up of the compound, so that, even if there is not sufficient available energy to affix new atoms, and, therefore, to characterise the

molecule as "unsaturated," there may be enough to make a stable compound with a similar molecule possible. For example, tetrabromotetraphenylethylene does not combine with bromine, but it does with acetone, carbon tetrachloride, benzene, etc.; that is, the ethylene carbon atoms possess insufficient energy for the former combination, but enough to attract molecules which are similarly possessed of slight available energy.

Tetraphenylethylene dichloride forms the following *molecular compounds*: with $2CHBr_3$, with $2CBr_4$, m. p. 144—147°, with $2CHBrCl_2$, with $2SO_2Cl_2$, glistening, transparent crystals. p-*Chlorotetraphenylethylene dichloride*, $C_6H_4Cl\cdot CPhCl\cdot CPh_2Cl$, m. p. 135—137°, obtained by the action of chlorine on the hydrocarbon (A., 1911, i, 31) yields the *compounds*: with $CHCl_3$, glistening cubes, m. p. 58—59°; with $2CCl_4$, m. p. 91—93°. Tetrabromotetraphenylethylene (*ibid.*) forms compounds: with $2COMe_2$, shining needles; with COMeEt; with $COEt_2$, long, lustrous needles; with CCl_4; with AcOEt; and with C_6H_6, large, lustrous needles. It also yielded a *dichloride*, m. p. 190—192°, but this did not combine with chloroform or carbon tetrachloride.

Triphenylcarbinol (X) forms a *compound*, $4X,3CCl_4$, large, flat squares, and a *compound*, $2X,COMe_2$, large, transparent prisms. Triphenylchloromethane forms *compounds*, with CCl_4, small, lustrous crystals, and with $\frac{1}{2}COMe_2$. J. C. W.

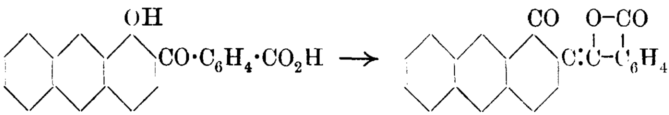
Formation of Liquid Hydrocarbons by the Action of Aluminium Chloride on Naphthalene under Pressure. FRANZ FISCHER [with WILHELM SCHNEIDER and SIEGFRIED HILPERT] (*Ber.*, 1916, **49**, 252—259).—In view of the fact that at present most of the naphthalene which is produced is only used as fuel, the author has attempted to prepare liquid hydrocarbons from it economically. For this purpose, catalytic hydrogenation is practically out of the question, owing to the amount of sulphur which is present, even in the technically pure product, and therefore experiments have been conducted on the degradation of naphthalene by means of aluminium chloride. It is found that about 40% of the naphthalene can be converted into an oil by heating it with 4% of its weight of aluminium chloride in an autoclave for a short time at about 330°. The remaining material is converted into pitch and coke.

A quantity of oil was obtained in this way, of which 79% distilled between 150° and 300°. This fraction deposited some naphthalene on cooling, but contained chiefly hydronaphthalenes. It had a calorific value of 9932, viscosity 1·16 at 20°, flash point 70—75°, and would serve as an illuminant in a burner with powerful air draught, such as is designed for Russian oils.

J. C. W.

Introduction of Acid Radicles into the Side Benzene Nuclei of Anthracene. Preparation of *o*-**1-Hydroxy-2-anthracoylbenzoic Acid.** ALFRED SCHAARSCHMIDT (*Ber.*, 1916, **49**, 381—385). —The hydrogen atoms in the central ring of anthracene are very

much more easily replaced than those in the outside rings, so that, for example, the introduction of acid radicles usually leads to *meso*-derivatives (compare A., 1915, i, 566). It has been found, however, that the hydroxyl group in 1-hydroxyanthracene has a very powerful orientating influence, so that condensation with phthalic anhydride in the presence of boric acid at 195—200° leads to the formation of o-1-*hydroxy-2-anthracoylbenzoic acid* (I). This was obtained in brownish-yellow crystals, m. p. 221°, which formed a very characteristic *ammonium* salt in sparingly soluble, golden-yellow crystals. The acid dissolved in concentrated sulphuric acid with a deep blue colour, which quickly changed to green, and the final solution deposited a brownish-red substance on dilution. The same compound was obtained by heating the acid with acetic anhydride and xylene in the hope of acetylating the acid, and it was recognised as the *lactone* of an o-*quinone* (II). It formed brownish-red leaflets, m. p. 246°.



(I.) (II.)

J. C. W.

Conversion of α-Methylnaphthalene into αβ-Di-α-naphthylethane and Picene. WALTER FRIEDMANN (*Ber.*, 1916, **49**, 277—284). —The author has studied the effect of heating α-methylnaphthalene with sulphur, and his results are shown to have an interesting bearing on the occurrence of picene and chrysene in brown-coal tar, for sulphur is a constant constituent of brown coal. The investigation will be extended in many directions.

From the product obtained by heating α-methylnaphthalene (24 grams) with sulphur (3 grams) at 300° for three days in a sealed tube, the following were isolated: a small amount of a *compound*, $S<\begin{matrix}C_{10}H_6\cdot CH_2\cdot S\\ C_{10}H_6\cdot CH_2\cdot S\end{matrix}$, silvery leaflets, m. p. 298—300° (*dipicrate*, slender, red needles, m. p. 240°), then αβ-di-α-naphthylethane (*dipicrate*, m. p. 205°), followed by α-dinaphthastilbene (Elbs, A., 1893, 271), and finally picene. J. C. W.

Preparation of Aromatic Nitroamino-compounds and their Substitution Products. H. POMERANZ (D.R.-P., 289454; from *J. Soc. Chem. Ind.*, 1916, **35**, 415).—Di- and polynitro-compounds are reduced to nitroamino-compounds by heating with iron filings and aqueous sulphuric acid until the iron is dissolved. The product may be obtained either directly, or after the removal of the sulphur dioxide by blowing in air, by either filtration, evaporation to dryness, or extraction with a suitable solvent. G. F. M.

The Supposed Isomerism of Formanilide. A. HANTZSCH [with JULIUS RETINGER] (*Ber.*, 1916, **49**, 232—234).—Orlov (A., 1905, i, 643) has described two new isomeric modifications of

formanilide, one being a liquid and the other having m. p. 245°. These new substances were obtained by heating aniline with glyceryl formate, and it is now shown that the liquid product is in reality very impure oxanilic acid, whilst the solid is oxanilide. The formation of these substances must have been due to the presence of oxalic acid or glyceryl oxalate in the formate, because pure glyceryl formate fails to react with aniline under the prescribed conditions.

D. F. T.

Aromatic Diglycines. SIGMUND FRÄNKEL and FELIX BRUCKNER (*Ber.*, 1916, **49**, 485—488).—Under suitable conditions, phenylenediglycines can be obtained from phenylenediamines and chloroacetic acid; for this purpose, the condensation must be effected in alkaline solution and between 80° and 120°, since at lower temperatures aminophenylglycines are formed, whilst above 120° methylaminophenylglycines and the anhydrides of diglycines result.

p-*Phenylenediglycine,* m. p. about 220°, is prepared by heating *p*-phenylenediamine with an aqueous solution of chloroacetic acid and sodium hydroxide on the water-bath. At the ordinary temperature a *substance,* m. p. 205°, is obtained, which is probably *p*-aminophenylglycine.

m-*Phenylenediglycine,* red, amorphous powder, m. p. 150°, is similarly prepared, and may also be obtained by condensation at the ordinary temperature if excess of alkali is used. The *sodium* salt, $C_{10}H_{10}O_4N_2Na_2$, m. p. 117°, is described. When heated above its melting point, *m*-phenylenediglycine appears to be converted into an intensely red anhydride.

o-*Phenylenediglycine* has m. p. 150°. In this case, if the condensation is performed at 120—150°, carbon dioxide appears to be eliminated and *methylaminophenyleneglycine* to be formed.

The diglycines yield green, amorphous *copper* salts and yellow *picrates.* When fused with alkali or similar condensing agents they give a blue dye, in quantity too small to permit of extended investigation.

H. W.

The Action of Primary Amines on Substances which Yield 1 : 3-Diketones. L. RÜGHEIMER (*Ber.*, 1916, **49**, 586—597. Compare Rügheimer and Ritter, A., 1912, i, 474; Rügheimer, A., 1915, i, 224).—It has been shown by Möhlau (A., 1895, i, 140) that two isomeric products are obtained by the action of ethyl acetoacetate on benzylamine in molecular proportions; the α-compound has m. p. 79—80° and the β-derivative m. p. 21—21·5°. The isomerides are interconvertible and are regarded as stereoisomeric forms of benzylaminocrotonic ester, $CH_2Ph\cdot NH\cdot CMe{:}CH\cdot CO_2Et$. This interpretation has been criticised by Hantzsch and von Hornbostel (A., 1898, i, 195), who consider the formulæ not to be established with sufficient definiteness to exclude other possibilities. The author is led to the conclusion that these substances represent an instance of keto-enolic tautomerism; the β-compound has the structure $CH_2Ph\cdot N{:}CMe\cdot CH{:}C(OH)\cdot OEt$, and, even in the molten

condition, does not appear to contain an appreciable quantity of the keto-form, thus differing sharply from the majority of similar compounds in which the carbonyl of the carbethoxy-group suffers enolisation. The α-compound represents the corresponding keto-form, $CH_2Ph\cdot N\colon CMe\cdot CH_2\cdot CO_2Et$.

The method of investigation is similar to that employed by the author in analogous cases (*loc. cit.*). In this instance, the introduction of acid radicles by the use of acid chlorides in the presence of water and alkali is not possible, since decomposition occurs with elimination of benzylamine; in the absence of water, however, the required compounds are readily obtained. Thus the p-*nitrobenzoyl* derivative of the β-compound,

$$CH_2Ph\cdot N\colon CMe\cdot CH\colon C(OEt)\cdot O\cdot CO\cdot C_6H_4\cdot NO_2,$$

pale yellow needles, m. p. 119—120°, is obtained in practically theoretical yield by adding a solution of *p*-nitrobenzoyl chloride in dry acetone to a solution of the β-compound in pyridine. It is readily decomposed by cold, fuming hydrochloric acid into *p*-nitrobenzoic acid and benzylamine, whilst under similar conditions the benzylamide of *p*-nitrobenzoic acid is not appreciably affected; decomposition with alcoholic potassium hydroxide follows a complicated course. The *anisoyl* derivative, m. p. 69—71°, is slowly decomposed by cold aqueous alcoholic potassium hydroxide, with the formation of anisic acid, whilst warm oxalic acid solution gives benzylamine hydrogen oxalate, m. p. 173° (decomp.), and a little anisic acid. When solutions of the *p*-nitrobenzoyl or anisoyl derivatives in absolute alcohol are treated with a trace of aqueous ferric chloride solution, a coloration cannot be observed after an hour; under similar conditions, the β-compound itself slowly gives a coloration, which deepens and finally disappears. With larger amounts of ferric chloride solution the anisoyl, but not the *p*-nitrobenzoyl derivative, soon yields a red colour, which gradually darkens. This result appears to be attributable to the amount of water used.

Attempts to prepare a *p*-nitrobenzoyl derivative of the α-compound are also described; the product, however, proved to be identical with the derivative of the β-compound described above even when reaction was effected at low temperatures.

When solutions of the α- and β-compounds in anhydrous ether are mixed with ethereal solutions of anhydrous ferric chloride under similar conditions, dark precipitates are produced, which dissolve on the addition of absolute alcohol with the production of red solutions, the intensity of the colour in which is identical after half an hour. Apparently the keto-form becomes enolised in the presence of solvents containing a hydroxyl group. When solutions of the two compounds in acetone, on the other hand, are mixed with ethereal solutions of ferric chloride, a difference is observed; the β-compound immediately gives a coloration which appears reddish-yellow by transmitted, deep brownish-red by reflected light, whilst the α-compound yields a precipitate resembling freshly-precipitated ferric hydroxide.

The following new substances have been incidentally obtained:

benzylamide of p-*nitrobenzoic acid*, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2Ph$, needles, m. p. 141—143°; *anisbenzylamide*, m. p. 131—132°.

H. W.

Amines. V. Formation of Schiff's Bases from β-Phenylethylamine and their Reduction to Alkyl Derivatives of this Amine. NORMAN A. SHEPARD and ARTHUR A. TICKNOR (*J. Amer. Chem. Soc.*, 1916, **38**, 381—387).—In connexion with a study of the relation between the chemical constitution and the therapeutic action of certain organic bases, the authors have prepared some *N*-substituted derivatives of β-phenylethylamine by reducing the benzylidene compounds of that base.

β-Phenylethylbenzylideneamine, $CH_2Ph\cdot CH_2\cdot N\colon CHPh$, crystallises in stout prisms, m. p. 41—42°, b. p. 188—189°/17—19 mm. (compare Barger and Walpole, T., 1909, **95**, 1723), and gives an almost quantitative yield of benzyl-β-phenylethylamine (Fischer, A., 1896, i, 262) on reduction with sodium and alcohol. *β-Phenylethylanisylideneamine* has m. p. 34—35°, b. p. 224—225°/17 mm., and p-*methoxybenzyl-β-phenylethylamine* is an oil which forms a *hydrochloride*, m. p. 266—267°. *β-Phenylethyl*-p-*hydroxybenzylideneamine* crystallises in clusters of pale yellow prisms, m. p. 188—190°, and p-*hydroxybenzyl-β-phenylethylamine*, obtained by reduction or by heating the above methoxy-compound with hydriodic acid, forms hexagonal tablets, m. p. 135—136°, and yields a *hydrochloride*, m. p. 225—226°, in clusters of long prisms. *β-Phenylethylsalicylideneamine* separates in yellow prisms, m. p. 45·5°, and o-*hydroxybenzyl-β-phenylethylamine* yields a *hydrochloride*, m. p. 130°, in prisms or blocks. β-Phenylethylvanillylideneamine crystallises in stout, yellow columns or prisms, m. p. 112—113° (compare Decker and Becker, A., 1913, i, 260), and p-*hydroxy*-m-*methoxybenzyl-β-phenylethylamine* forms needles, m. p. 99—100°, and yields a *hydrochloride*, in clusters of slender needles, m. p. 180°.

J. C. W.

A Compound of Nitrogen with Five Hydrocarbon Radicles. W. SCHLENK and JOHANNA HOLTZ (*Ber.*, 1916, **49**, 603—608).—Since the triphenylmethyl group possesses the remarkable properties of forming stable compounds with the alkali metals, the authors have attempted to isolate the corresponding derivative containing the somewhat similar tetramethylammonium group. For this purpose, a solution of sodium triphenylmethyl in ether is shaken with dried tetramethylammonium chloride, the operation being conveniently effected in the apparatus described by Schlenk and Thal (A., 1913, i, 1205). In the course of a few minutes the solution becomes nearly decolorised, and a dark chrome-red precipitate of *triphenylmethyltetramethylammonium*, $CPh_3\cdot NMe_4$, separates. The ethereal solution is decanted, the residue repeatedly washed with ether, dissolved in pyridine, and, after filtration, the required product is precipitated by addition of ether.

Triphenylmethyltetramethylammonium forms a red, crystalline mass with a blue metallic glance. It is immediately decomposed

by water into triphenylmethane and tetramethylammonium hydroxide; carbon dioxide converts it into tetramethylammonium triphenylacetate. It is very sensitive to oxygen, but the course of the action has not yet been completely investigated. It is insoluble in ether or benzene, soluble in pyridine to a blood-red solution, which appears to contain a labile additive product. The solution conducts electricity, so that the triphenylmethyl group appears to take the position and fulfil the function of the acid group in the ordinary ammonium salts.

A solution of sodium triphenylmethyl slowly reacts with ammonium chloride, forming triphenylmethane and sodamide in accordance with the equations $CPh_3Na + NH_4Cl = NaCl + CHPh_3 + NH_3$ and $CPh_3Na + NH_3 = CHPh_3 + NaNH_2$.

H. W.

Nitrosoarylhydroxylamines. I. The Influence of Nuclear Substitution on Groups which give rise to Internally Complex Salts. OSKAR BAUDISCH (*Ber.*, 1916, **49**, 172—180).—A discussion of the relative behaviour of the nitrosoarylhydroxylamines, dealing with the effect produced by substitution in the aromatic nucleus on the power to form internally complex salts and on the selective action of the substance in forming such salts only with certain metals.

Nitrosophenylhydroxylamine forms characteristic, internally complex salts with iron, copper, titanium, and zirconium (Bamberger and Baudisch, A., 1909, i, 977; Baudisch, A., 1910, ii, 76; Thornton, A., 1914, ii, 299, 583), this power being unaffected by the introduction of the groups $\cdot Cl$, $\cdot Br$, $\cdot NO_2$, $\cdot Me$, and $\cdot OMe$ into the aromatic nucleus. If, however, one of the groups $\cdot O\cdot SO_2\cdot C_6H_4Me$, $\cdot OH$, $\cdot NH\cdot SO_2\cdot C_6H_4Me$, $\cdot NMe\cdot SO_2\cdot C_6H_4Me$, $\cdot NMe_2$, and $\cdot CHO$ is introduced at the ortho- or meta-position, the behaviour of the substance in forming internally complex salts is altered. *o*-Nitrosohydroxylaminophenyl 4-toluenesulphonate, $OH\cdot N(NO)\cdot C_6H_4\cdot O\cdot SO_2\cdot C_6H_4Me$, yields internally complex salts with almost all metals (see Baudisch, Gurewitsch, and Rothschild, following abstract), and the corresponding 2-toluenesulphonate exhibits similar behaviour. In order to ascertain whether the sulphur atom is responsible for this alteration, the behaviour of nitroso-*o*-methoxyphenylhydroxylamine was examined, with the discovery that this substance in character closely resembles the parent nitrosophenylhydroxylamine, although of slightly more marked power to form complex salts; however, nitroso-*o*-hydroxyphenylhydroxylamine has the power to form complex salts with almost all metals. It would therefore appear that whereas in the methoxy-group the oxygen atom possesses little residual affinity, on account of its load, the oxygen atom in the hydroxyl group is more active, whilst in the toluenesulphonates the two doubly linked oxygen atoms of the sulpho-group have considerable residual affinity, and so are able to impart to the molecule marked power to form complexes.

In support of this view, the following further evidence is

adduced. *m*-4-Toluenesulphonylaminonitrosophenylhydroxylamine, $OH \cdot N(NO) \cdot C_6H_4 \cdot NH \cdot SO_2 \cdot C_6H_4Me$, and its methyl derivative, $OH \cdot N(NO) \cdot C_6H_4 \cdot NMe \cdot SO_2 \cdot C_6H_4Me$, form internally complex salts with almost all metals, the products resembling in colour and solubility the salts derived from the above *o*- and *p*-toluenesulphonates, whilst nitroso-*m*-dimethylaminophenylhydroxylamine, $NMe_2 \cdot C_6H_4 \cdot N(NO) \cdot OH$, gives complex salts quite different from some of the preceding; thus its copper salt is canary-green, whereas the copper salts of the other compounds mentioned are grey or greyish-blue. Nevertheless, the dimethylamino-compound yields internally complex salts with almost all metals, the nitrogen atom being the probable seat of the necessary residual affinities; in the two toluenesulphonylamino-compounds the nitrogen is heavily weighted, and the residual affinity of the molecule is mainly centred at the doubly linked oxygen atoms. In an analogous manner, *nitroso-o-aldehydophenylhydroxylamine* contains a doubly linked oxygen atom and also gives internally complex salts with various metals, the copper compound being greyish-blue.

Thus it is possible by the introduction of suitable substituents to influence the selective character of the group responsible for complex salt formation.

The residual affinities of the parent substances are not completely saturated in the complex salts, because these are able to form additive compounds with new molecules, for example, with acids, bases, or neutral salts; thus the copper salt of nitrosophenylhydroxylamine when dissolved in xylene combines with hydrogen chloride, yielding a grass-green complex salt, which slowly eliminates the latter constituent on exposure to the air or when moistened with water.

Attention is drawn to the probable value of investigations of such complex salts as reagents for analytical chemistry and as drugs in physiological chemistry. Thus it is reported that in the treatment of psoriasis with various hydroxyanthracene, hydroxyanthranol, and hydroxyanthraquinone derivatives, only those hydroxyanthranol compounds possessed marked anti-psoriatic effect in which the hydroxyl radicle occupied the peri-position relative to the carbonyl group; this result appears to stand in connexion with the observation of Pfeiffer (A., 1913, i, 879) that only hydroxyl groups in the ortho-position to a carbonyl group are effective in imparting the power to form complex salts. Likewise it is noteworthy in the case of salvarsan that of the numerous aromatic arsenic compounds, the most marked physiological action is possessed by the member which contains a grouping markedly favourable to the formation of internally complex salts, namely, an amino-group in the ortho-position to a hydroxyl group.

D. F. T.

Nitrosoarylhydroxylamines. II. Internally Complex Metallic Salts of *o*-Nitrosohydroxylaminophenyl 4-Toluenesulphonate. OSKAR BAUDISCH, H. GUREWITSCH, and S. ROTHSCHILD (*Ber.*, 1916, **49**, 180—190. Compare preceding abstract).—The ammonium salt

of *o*-nitrosohydroxylaminophenyl 4-toluenesulphonate, already described by Baudisch and Karzeff (A., 1912, i, 441), dissolves in pure water to a clear solution, but so readily does it give bulky precipitates with salts of other metals that with ordinary water a thick turbidity is produced. By double decomposition in aqueous solution the salts described below were obtained. These are quite generally insoluble in water, but soluble in many organic solvents; they possess the power of combining with further substances, acids, bases, or salts, with simultaneous alteration in colour or in solubility.

The *cobalt* salt is a pale, rose-coloured, crystalline powder soluble in chloroform, benzene, toluene, acetone, alcohol, ethyl acetate, ammonia, and pyridine. *Nickel* salt, green crystals, resembling the cobalt salt in solubility. *Ferric* salt, yellow crystals. *Chromium* salt, grey crystals. *Uranyl* salt, deep yellow. *Lead* salt, colourless needles. *Bismuth* salt, pale yellow, crystalline powder. *Mercuric* salt, yellow crystals. *Cerium* salt, yellow. *Lanthanum* salt, colourless needles. *Thorium* salt, colourless. *Aluminium* salt, colourless. *Cadmium* salt, colourless. *Copper* salt, greyish-blue.

To all the above salts is ascribed the constitution

$$C_6H_4Me\cdot SO_3\cdot C_6H_4\cdot N\lessdot{}^{NO}_{O}\gtrdot X,$$

where X represents an equivalent weight of the metal (see Bamberger and Baudisch, A., 1909, i, 977). D. F. T.

Nitrosoarylhydroxylamines. III. Internally Complex Metallic Salts. OSKAR BAUDISCH, A. E. PISTOR, and B. SILBERBLATT (*Ber.*, 1916, **49**, 191—202. Compare preceding abstracts).—o-*Nitrosohydroxylaminophenyl 2-toluenesulphonate*,

$$OH\cdot N(NO)\cdot C_6H_4\cdot O\cdot SO_2\cdot C_6H_4Me,$$

was prepared by treating *o*-nitrophenol in alcoholic solution with sodium ethoxide and *o*-toluenesulphonyl chloride, the resulting o-*nitrophenyl 2-toluenesulphonate*, colourless leaflets, m. p. 131—134°, being then reduced in alcoholic solution with ammonium sulphide to o-*hydroxylaminophenyl 2-toluenesulphonate*, prisms, m. p. 61°; this on treatment with dry ammonia and amyl nitrite in ethereal solution gave the nitroso-compound as its *ammonium* salt, colourless needles, m. p. 118—122° (decomp.). By interaction of aqueous solutions of the ammonium salt and inorganic salts of various metals, the following internally complex salts were obtained: *copper* salt, greyish-blue; *lead* salt, colourless needles; *cobalt* salt, reddish-white powder; *nickel* salt, very pale green crystals; *neodymium* salt, blue crystals; *lanthanum* salt, colourless; *praseodymium* salt, colourless crystals; *erbium* salt, colourless; *yttrium* salt, colourless; *thorium* salt, colourless; *magnesium* salt, colourless. In the general manner of internally complex salts, these compounds are very sparingly soluble in water but soluble in organic solvents; they show only slight differences from the corresponding derivatives of the isomeric *p*-toluenesulphonates (preceding abstract) in solubility.

Nitroso-4-toluenesulphonyl-m-*aminophenylhydroxylamine*,

$$C_6H_4Me\cdot SO_2\cdot NH\cdot C_6H_4\cdot N(NO)\cdot OH,$$

prepared in a similar manner to the preceding through 4-*toluenesulpho*-m-*nitroanilide*, m. p. 138—140°, and m-4-*toluenesulphonylaminophenylhydroxylamine*, colourless leaflets, was first obtained as the *ammonium* salt, m. p. 165° (decomp.), from which the free substance, almost colourless scales, m. p. 109—111°, was liberated by treatment in aqueous solution with metaphosphoric acid in the presence of ether.

The complex salts were prepared in the usual manner. *Ferric* salt, reddish-brown; *copper* salt, blue; *cobalt* salt, rose-coloured; *nickel* salt, green.

Nitroso-m-4-*toluenesulphonylmethylaminophenylhydroxylamine*, $C_6H_4Me\cdot SO_2\cdot NMe\cdot C_6H_4\cdot N(NO)\cdot OH$, was prepared by treating 4-toluenesulpho-*m*-nitroanilide with methyl sulphate, and reducing the resulting 4-*toluenesulpho*-m-*nitromethylanilide*, colourless needles, m. p. 111°, to m-4-*toluenesulphonylmethylaminophenylhydroxylamine*, colourless needles, m. p. 119°, which was convertible by the action of ammonia and amyl nitrite into the colourless *ammonium* salt, decomp. 134—148°, of the required substance. *Lead* salt, colourless; *nickel* salt, very pale green crystals; *cobalt* salt, reddish-grey crystals; *chromium* salt, yellow; *yttrium* salt, colourless; *aluminium* salt, colourless. D. F. T.

Nitrosoarylhydroxylamines. IV. Internally Complex Metallic Salts. OSKAR BAUDISCH and H. ROM (*Ber.*, 1916, **49**, 203—210. Compare Baudisch, preceding abstracts).—A description of the internally complex salts derived from nitroso-*m*-dimethylaminophenylhydroxylamine, $NMe_2\cdot C_6H_4\cdot N(NO)\cdot OH$, with various metals. The salts are all of the internally complex type, insoluble in water, but readily soluble in most organic solvents.

m-Nitrodimethylaniline by reduction in alcoholic solution with ammonia and hydrogen sulphide was converted into m-*dimethylaminophenylhydroxylamine*, $NMe_2\cdot C_6H_4\cdot NH\cdot OH$, an unstable, yellow mass, m. p. 107—108°, which reduces Fehling's solution and ammoniacal silver nitrate, and, like phenylhydroxylamine, causes sneezing. When treated in cold ethereal solution successively with ammonia and amyl nitrite, the compound yields the *ammonium* salt of *nitroso*-m-*dimethylaminophenylhydroxylamine*,

$$NMe_2\cdot C_6H_4\cdot N(NO)\cdot ONH_4,$$

as lustrous, white needles, the alcoholic solution of which on evaporation yields reddish-violet needles of characteristic odour. By double decomposition between the ammonium salt and various inorganic salts in aqueous solution, the following internally complex salts were obtained: *copper* salt, canary-green precipitate; *ferric* salt, deep brown; *nickel* salt, green, silky crystals; *thorium* salt, yellowish-white; *cobalt* salt, flesh-red precipitate, decomp. near 110°; *praseodymium* salt, amorphous, colourless solid, decomp. at 145°; *neodymium* salt, yellowish-green; *lanthanum* salt, yellow.

D. F. T.

Preparation of Mixed Carbamides and Thiocarbamides of the Aromatic Series. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P., 289163; from *J. Soc. Chem. Ind.*, 1916, **35**, 438).—Mixed carbamides or thiocarbamides are obtained when two different aromatic amino-acids, at least one of which belongs to the naphthalene series, having amino-acid residues substituted in their amino-groups, are treated in molecular proportions with carbonyl chloride or thiocarbonyl chloride, or a substitute for these (compare A., 1915, i, 14). The compounds obtained are mostly yellow to brown in colour, and are precipitated from aqueous solution by sodium chloride or alcohol. Those containing free hydroxyl groups yield azo-dyes when coupled with diazonium compounds. G. F. M.

Preparation of Carbamides and Thiocarbamides of the Naphthalene Series. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P., 289270, 289271, 289272; from *J. Soc. Chem. Ind.*, 1916, **35**, 438).—Instead of starting with the materials described in the chief patent (D.R.-P., 278122; A., 1915, i, 14), the method there described is applied to the naphthylaminesulphonic acids substituted in the amino-group by aromatic aminoacidyl radicles, other than those of the benzene series. Moreover, thiocarbonyl chloride may be used instead of carbonyl chloride, so as to produce thiocarbamides. In the case of the di- and poly-sulphonic acids, the sodium salts are used. The new carbamides and thiocarbamides are white or brown powders having valuable therapeutic properties. The second patent substitutes other aminoacylated aminonaphtholsulphonic acids for the 1:8-aminonaphtholsulphonic acids of the principal patent, such as, for example, *p*-aminobenzoyl-2-amino-8-naphthol-3:6-disulphonic acid and numerous others. The products are strongly destructive to blood parasites. The third patent describes the above condensation using aminonaphthalenesulphonic acids substituted in the amino-group by the aminophenylcarbamide radicle. The di- and poly-sulphonic acids form acid and normal sodium salts, the latter being the more soluble. Their diazo-derivatives coupled with R-salt give yellowish-red to bluish-red dyes. G. F. M.

The Products of the Decomposition of Aluminium Phenoxides by Heat. RICHARD MÖHLAU (*Ber.*, 1916, **49**, 168—171).—Gladstone and Tribe (this Journal, 1876, i, 158; T., 1881, **39**, 1) have observed that, when heated, the aluminium phenoxides decompose, yielding aluminium oxide, benzene hydrocarbons, phenols, phenolic ethers, and small quantities of a substance of the composition $C_{13}H_{10}O$ or homologous to this. The author states that the decomposition of aluminium phenoxide may be approximately represented $4Al(OPh)_3 = 2Al_2O_3 + 10C + H_2 + CH_4 + C_6H_6 + 3Ph{\cdot}OH + 2Ph_2O + C_{13}H_{10}O$, and finds that the last substance is xanthene, produced by the pyrogenic conversion of methane and phenol into cresol, which by condensation with phenol to *o*-dihydroxydiphenylmethane passes easily into xanthene.

Similarly, the unidentified products, $C_{15}H_{14}O$, obtained by Glad-

stone and Tribe from aluminium *p*-tolyloxide, aluminium *o*-tolyloxide, and aluminium thymoxide are probably 2:7-dimethylxanthene, 4:5-dimethylxanthene, and 3:6-dimethylxanthene respectively. D. F. T.

Preparation of β-Orcinol. ADOLF SONN (*Ber.*, 1916, **49**, 621—623).—*Dinitro*-p-*acetoxylidide*, $C_6H(NO_2)_2Me_2\cdot NHAc$, is prepared by the gradual addition of aceto-*p*-xylidide to cold fuming nitric acid. It forms fine white needles, m. p. 228° (uncorr.), and yields the corresponding *amine*, yellowish-brown needles, m. p. 202—203°, when boiled with alcohol and dilute sulphuric acid. When the latter is gradually added to a well-cooled solution of sulphur dioxide in concentrated nitric acid, and the mixture poured on to ice and subsequently warmed with alcohol and copper sulphate, dinitro-*p*-xylene, m. p. 124°, separates quantitatively, and can be used for the preparation of β-orcinol. H. W.

Organic Periodides. I. Periodides of Phenacetin, Methacetin, and Triphenin. W. O. EMERY (*J. Amer. Chem. Soc.*, 1916, **38**, 140—150).—In connexion with the development of a scheme for drug analysis, the author decided to study the iodine-additive products of the important synthetic drugs, especially with a view of effecting a quantitative separation of phenacetin and acetanilide. It was found that the literature contained references to a product of the action of iodine, potassium iodide, and hydrochloric acid on phenacetin, which was patented under the name of "iodophenin" (Scholvien, 1891, and Riedel, D.R.-P., 58409). This has been applied to the purpose indicated above (A., 1914, ii, 755), but it is now shown that the accepted ideas about its constitution are quite erroneous. Relying only on an estimation of the amount of iodine in it which will react with thiosulphate, it was accorded the formula $OEt\cdot C_6H_4\cdot NAcI_2\cdot NHAcI\cdot C_6H_4\cdot OEt$, but it is really a periodide of a hydriodide, thus, $(OEt\cdot C_6H_4\cdot NHAc)_2,HI,I_4$. Piutti in 1895 obtained a similar compound from methacetin (acetanisidide), and gave it the formula $(OMe\cdot C_6H_4\cdot NHAc)_2I_3$, but this is really $(OMe\cdot C_6H_4\cdot NHAc)_2,HI,I_2$. The rôle of the free hydriodic acid in the reaction had been overlooked.

The under-mentioned hydriodides were prepared by the action of dry hydrogen iodide on dry, alcohol-free solutions of the "bases," and the periodides were obtained either by treating these with the requisite amount of iodine or by treating the bases with iodine and hydriodic acid or iodine, potassium iodide, and hydrochloric acid. p-*Acetophenetidide hydriodide*, $(OEt\cdot C_6H_4\cdot NHAc)_2,HI$, forms colourless needles, m. p. 147—148°; the *hydriododi-iodide*, $(C_{10}H_{13}O_2N)_2,HI,I_2$, is occasionally obtained by observing special conditions as reddish-brown crystals, m. p. 124—125°; the *hydriodotetraiodide* (so-called "iodophenin"), $(C_{10}H_{13}O_2N)_2,HI,I_4$, separates in reddish-brown leaflets or steely-blue, prismatic needles, m. p. 133—134°. *Acetanisidide hydriodide*,

$$(OMe\cdot C_6H_4\cdot NHAc)_2,HI,$$

has m. p. 125—127°; the *hydriododi-iodide*, $(C_9H_{11}O_2N)_2,HI,I_2$, crystallises in various forms and shades of reddish-brown, according to the solvent, etc., and has m. p. 142—143°. *p*-Propiophenetidide (triphenin) hydriodide seems to be soluble in organic media, but the *hydriododi-iodide*, $(C_{11}H_{15}O_2N)_2,HI,I_2$, separates in greenish-bronze needles, m. p. 121—123°, and the *hydriodotetra-iodide*, $(OEt{\cdot}C_6H_4{\cdot}NH{\cdot}COEt)_2,HI,I_4$, forms purple-black, silky needles, m. p. 92—94°. J. C. W.

A New Case of Tautomerism. 1 : 4 : 5 : 6-Tetrahydroxynaphthalene. A. S. WHEELER and V. C. EDWARDS (*J. Amer. Chem. Soc.*, 1916, **38**, 387—393).—Zincke and Schmidt (A., 1895, i, 613) obtained 1 : 4 : 5 : 6-tetrahydroxynaphthalene by the reduction of 5 : 6-dihydroxy-α-naphthaquinone ("naphthazarin"), and noticed that the original yellow crystals changed into a red substance of the same composition when the solutions were exposed to the air, particularly on heating. They assumed that the change of colour was due to the presence of a small amount of an oxidation product. In view of the fact that the trihydroxynaphthalene, α-juglone, readily changes into a ketonic form (Willstätter and Wheeler, A., 1915, i, 268), the present authors have sought to establish similar tautomerism between the two forms of the tetrahydro-compound. They find that, besides forming a tetra-acetate, both forms react with the less basic of the ketone reagents, yielding with phenylsemicarbazide even a diphenylsemicarbazone. It has been impossible to isolate definitely a keto or enol form, however, and it cannot be said that the red and yellow substances differ chemically. The form of tautomerism exhibited seems to be like that of phloroglucinol, in which only one isomeride, with both ketonic and phenolic properties, can be recognised.

Commercial naphthazarin was purified by sublimation in a vacuum and reduced by means of stannous chloride and aqueous hydrochloric acid. The 1 : 4 : 5 : 6-tetrahydroxynaphthalene so obtained gave an impure *semicarbazone*, a *phenylsemicarbazone*, $C_{17}H_{15}O_4N_3$, fan-like groups of stout, yellow needles, m. p. 218° (decomp., violet vapours); an impure *diphenylsemicarbazone*, hexagonal plates, which darkened at 280°; a p-*bromophenylsemicarbazone*, $C_{17}H_{14}O_4N_3Br$, yellow needles, decomp. 220—223°; a p-*nitrophenylsemicarbazone*, $C_{16}H_{13}O_5N_3$ [?], yellow needles or prisms, which gave violet fumes at about 241°; a *benzhydrazone*, $C_{17}H_{14}O_4N_2$, yellow needles, decomp. 170—185°; and a p-*nitrobenzhydrazone*, $C_{17}H_{13}O_6N_3$, yellow needles, m. p. 220—224° (decomp.). Attempts were made to methylate the compound by means of methyl sulphate, diazomethane, and methyl alcohol mixed with sulphuric acid. A *monomethyl ether*, $C_{11}H_{10}O_4$, reddish-yellow needles, m. p. 115—140°, was apparently obtained under the last conditions. J. C. W.

Ortho-substituted Xylyltellurium Compounds. KARL LEDERER (*Ber.*, 1916, **49**, 334—344).—Two ortho-substituted tellurides, namely, di-*p*-xylyl and di-*m*-4-xylyl telluride, have been prepared,

and their behaviour towards halogens has been studied in extension of the investigation of the phenyl and tolyl tellurides (A., 1912, i, 852).

Di-p-*xylyl telluride*, $Te(C_6H_3Me_2)_2$, was prepared by the action of tellurium dibromide on magnesium *p*-xylyl bromide, and separated from the accompanying di-*p*-xylyl by distillation. It formed silky needles, m. p. 72°, b. p. 260—275°/34 mm., and combined directly with the halogens in ethereal solution. *Di*-p-*xylyltelluronium dichloride*, $TeCl_2(C_6H_3Me_2)_2$, crystallised in small, colourless needles, m. p. 197—198°; the *dibromide*, in yellow needles, m. p. 189—190°; and the *di-iodide*, in deep reddish-brown needles, m. p. 161—162°. The dibromide yielded *di*-p-*xylyltelluronium oxide*, $TeO(C_6H_3Me_2)_2$, a microcrystalline powder, m. p. 225—226°, when heated with dilute sodium hydroxide. When boiled with water, the dichloride and dibromide were gradually hydrolysed, but it was not possible to obtain basic products; a *compound*, m. p. 227°, which approximates to the constitution of an anhydride of $C_{16}H_{18}TeCl{\cdot}OH$, and reacts with potassium iodide to give the corresponding iodine derivative, is described. The telluride also combined with methyl iodide to form *di*-p-*xylylmethyltelluronium iodide*, $TeMeI(C_6H_3Me_2)_2$, m. p. 137° (decomp.), from which the *picrate*, m. p. 170°, was prepared. Double salts with mercuric haloids were also obtained: *mercurichloride*, $Te(C_6H_3Me_2)_2HgCl_2$, columns, m. p. 179—180°; *mercuribromide*, broad needles, m. p. 169—170°; *mercuri-iodide*, golden-yellow needles, m. p. 166—167°.

Di-m-4-*xylyl telluride* was obtained as a faintly yellow oil, b. p. 202—203°/10 mm., by treating magnesium *m*-xylyl bromide with tellurium dibromide, converting the crude telluride into its dibromide, and reducing this again by means of magnesium methyl iodide. The following derivatives were prepared: *dichloride*, microscopic columns, m. p. 187—188°; *dibromide*, microscopic, yellow prisms, m. p. 200—201°; *di-iodide*, ruby-red columns, m. p. 181—182°; *mercurichloride*, m. p. 106°; *mercuribromide*, m. p. 99°; *mercuri-iodide*, yellow scales, m. p. 107—108°; *di*-m-4-*xylyltelluronium oxide*, m. p. 216—217°; and the product of the action of boiling water on the dichloride, namely, the anhydride of the *basic chloride*, $(C_{16}H_{18}TeCl)_2O$, m. p. 239—240°. J. C. W.

Mesityltellurium Compounds. KARL LEDERER (*Ber.*, 1916, **49**, 345—349).—*Dimesityl telluride*, $Te(C_6H_2Me_3)_2$, was obtained by the action of tellurium dibromide on magnesium mesityl bromide in crystals, m. p. 129°, and converted into the following telluronium compounds: *dichloride*, needles, m. p. 178—179°; *dibromide*, small, yellow needles, m. p. 205—206° (decomp.); *di-iodide*, very deep red columns, m. p. 111°; *oxide*, $TeO(C_6H_2Me_3)_2$, m. p. 204—205°; and *anhydride* of a *basic iodide*, $(C_{18}H_{22}TeI)_2O$, m. p. 100°.

J. C. W.

Hydrogenation of Esters of Nitrobenzoic Acid in Acid Solution. Preparation of Esters of Hydrazobenzoic Acid. WALTER KRÖSCHE (*Chem. Zentr.*, 1915, ii, 1186; from *Arbeit. Pharm. Inst. Univ. Berlin*, 1914, **11**, 95).—The idea that the

reduction of aromatic nitro-compounds in acid solution yields amines directly is not entirely correct. The esters of *p*-nitrobenzoic acid when reduced with zinc dust and acetic acid give a mixture of esters of hydrazo- and amino-benzoic acids, whilst nitrobenzene will yield up to 10% of azobenzene. For the separation of the esters use was made of the relatively difficult hydrolysis of those of the amino-acid.

The following esters were obtained: ethyl *p*-hydrazobenzoate (compare Meyer and Dahlem, A., 1903, i, 448), colourless needles, m. p. 118°, which redden in the air; *menthyl* p-*hydrazobenzoate*, small, colourless crystals, m. p. 131°, which redden in the air; *menthyl* p-*aminobenzoate*, compact, colourless crystals, m. p. 85—86°. D. F. T.

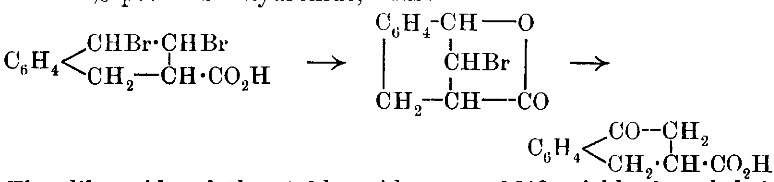
The Structure of the Dihydro-β-naphthoic Acids. C. G. DERICK and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1916, **38**, 400—419).—Sowinski (A., 1891, 1381), and Baeyer and Besemfelder (A., 1892, 191), obtained two of the three possible dihydro-β-naphthoic acids (having the unsaturated linking in the same ring as the carboxyl group) by the reduction of β-naphthoic acid with sodium amalgam. One of these was readily transformed into the other, and yielded a dibromide, which decomposed spontaneously into a monobromolactone. For these reasons, and because Pickard and Yates (T., 1909, **95**, 1011—1015) succeeded in resolving it into optically active components, it must be 1:2-dihydro-β-naphthoic acid. The third isomeride has now been obtained by boiling either of the older acids with barium hydroxide under pressure or with potassium hydroxide. From a study of the three dibromides and of the oxidation of the new acid, the constitutions of the acids are now completely established. The older stable acid is 1:4-dihydro-β-naphthoic acid, and the new acid is the 3:4-isomeride.

β-Naphthoic acid was obtained on a fairly large scale by sulphonating naphthalene and isolating the β-isomeride by Witt's method (A., 1915, i, 515), then distilling the sodium sulphonate with potassium ferrocyanide under reduced pressure and hydrolysing the nitrile. The acid was reduced with sodium amalgam and the product separated into its components by fractional precipitation, the labile acid being further purified by reducing its dibromide. The new acid was then prepared from these as indicated above.

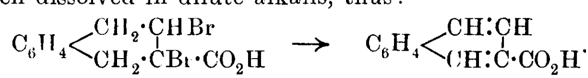
The old stable 1:4-dihydro-β-naphthoic acid has m. p. 161°, the labile 1:2-acid has m. p. 101·2°, and the new 3:4-*dihydro-β-naphthoic acid*, $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ CH{=}C\cdot CO_2H\end{matrix}$, crystallises in clusters of radiating needles, m. p. 118°. Of the stable acids, the new one is the more difficult to rearrange, and is about twice as soluble as the other in water, the temperature-coefficients for the range 0—97° being about the same, however. The dibromides were prepared in the usual way, chloroform being the appropriate solvent. 3:4-Dibromo-1:2:3:4-tetrahydro-β-naphthoic acid, m. p. 172° (decomp.), from the labile acid was not found to be liable to undergo

spontaneous decomposition; the new 1:2-*dibromo*-1:2:3:4-*tetrahydro-β-naphthoic acid* forms white crystals, m. p. 190° (decomp.). The following amides were also prepared for comparison: *β-naphthamide*, m. p. 195°; *tetrahydro-β-naphthamide*, m. p. 137°; 1:2-*dihydro-β-naphthamide*, m. p. 140—150°; the 1:4-*isomeride*, m. p. 168°; the 3:4-*isomeride*, m. p. 155°; and cinnamamide, m. p. 148°. It is pointed out that the two stable dihydro-acids give amides which exhibit the cinnamon-like odour of cinnamamide, a property which is characteristic of the grouping $=C\colon C-C\colon O$.

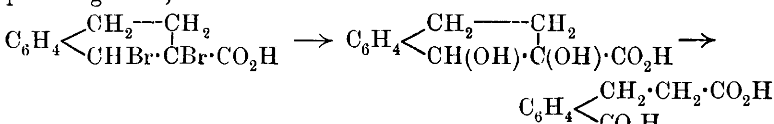
The behaviour of the dibromides towards alkalis affords a clue to their constitution. The dibromide of the labile acid dissolves in 5% sodium carbonate, forming the monobromolactone, and this is transformed into 4-*keto*-1:2:3:4-*tetrahydro-β-naphthoic acid*, m. p. 143—145° [*semicarbazone*, m. p. 266° (decomp.)], on boiling with 20% potassium hydroxide, thus:



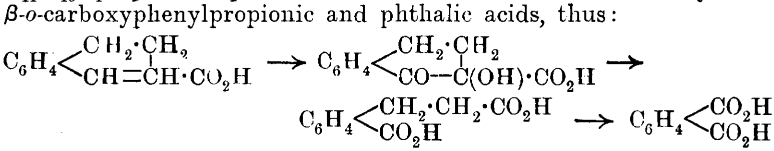
The dibromide of the stable acid, m. p. 161°, yields β-naphthoic acid when dissolved in dilute alkalis, thus:



The dibromide of the new acid yields 1:2-*dihydroxy*-1:2:3:4-*tetrahydro-β-naphthoic acid*, white plates, m. p. 182°, which forms β-*o*-carboxyphenylpropionic acid on oxidation with alkaline permanganate, thus:



The oxidation of the new acid was also carried out in stages by means of alkaline permanganate. The first product was apparently a hydrate of 2-*hydroxy*-1-*keto*-1:2:3:4-*tetrahydronaphthoic acid*, $C_{11}H_{10}O_4,H_2O$, m. p. 119—120°, and further oxidation yielded β-*o*-carboxyphenylpropionic and phthalic acids, thus:



(All the m.p.'s are "corrected.") J. C. W.

The Structure of the Dihydro-α-naphthoic Acids. Oliver Kamm and Harry Bruce McClugage (*J. Amer. Chem. Soc.*, 1916, **38**, 419—430).—Of the three possible dihydro-α-naphthoic acids

with the unsaturated linking in the same ring as the carboxyl group, two have been obtained by the reduction of α-naphthoic acid with sodium amalgam (Sowinski, A., 1891, 1380; Baeyer and Schoder, A., 1892, 191). The third has not yet been obtained, but a study of the dibromides of the known acids along the lines followed in the case of the β-acids (previous abstract) has established the structure of these. The labile acid, m. p. 86·5°, is 1:4-dihydro-α-naphthoic acid, and the stable one, m. p. 121·5°, is 3:4-dihydro-α-naphthoic acid.

α-Naphthoic acid was prepared from α-naphthylamine through the nitrile, and reduced as indicated. The labile acid obtained was converted into the stable one by boiling with 5% potassium hydroxide for half an hour, and both were purified until the ionisation constants were satisfactory. The dibromides were prepared in the usual manner, and then treated with 5% potassium hydroxide. The dibromide of the labile acid, m. p. 125°, yielded α-naphthoic acid and a little naphthalene, whilst the dibromide of the stable acid, m. p. 151° (decomp.), gave an acidic, coloured substance and 1:2-*dihydroxy*-1:2:3:4-*tetrahydro-α-naphthoic acid*, white plates, m. p. 175° (decomp.), thus:

$$C_6H_4{<}\begin{matrix}CH_2\text{———}CH_2\\ CBr(CO_2H)\cdot CHBr\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH_2\text{————}CH_2\\ C(OH)(CO_2H)\cdot CH\cdot OH\end{matrix}.$$

An attempt to prepare the third isomeride involved the reduction of 4-ethoxy-α-naphthoic acid (future communication) without losing the ethoxy-group, but this could not be effected. J. C. W.

ω-Sulphonic Acids of *p*-Aminophenyl Salicylate and their Derivatives. I. J. Abelin and M. Perelstein (*Annalen*, 1916, **411**, 216—229).—Of the three methods of preparing ω-sulphonic acids of amines of the type $NHR\cdot CHR'\cdot O\cdot SO_2H$ (R = alkyl or aryl; R′ = hydrogen, alkyl, or aryl), those of Schiff (1866) and of Miller and Plöchl (1891) are inconvenient or restricted in their application, the best being Eibner's method (1901) of condensing amines with the bisulphite compounds of aldehydes (and ketones). The researches of Reinking, Dehnel, and Labhardt (A., 1905, i, 261), Bucherer (A., 1906, i, 828; ii, 741), and Knoevenagel (A., 1904, i, 994) indicate that these ω-sulphonic acids are really sulphurous esters; evidence in the same direction is also afforded by the bactericidal and pharmacological action of the new compounds now to be described.

p-Aminophenyl salicylate reacts much more sluggishly than aniline, toluidines, etc., with aldehyde bisulphite compounds, the solution requiring prolonged boiling to ensure the formation of the ω-sulphonic acid; in many cases the addition of sodium acetate accelerates the reaction. The *sodium ω-methylsulphonate*,

$$OH\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot NH\cdot CH_2\cdot O\cdot SO_2Na,H_2O,$$

prisms or needles, decomp. 228°, is obtained by heating *p*-aminophenyl salicylate, formaldehyde, sodium hydrogen sulphite, and sodium acetate in aqueous alcohol. Its aqueous solution has a yellow colour and neutral reaction, develops a reddish-violet colora-

tion with ferric chloride, and reduces ammoniacal silver oxide solution. The *potassium* salt, leaflets, with $1H_2O$; *lithium*; and *calcium* salt, with $2H_2O$, are mentioned. The free *acid*, colourless needles, with $1H_2O$, has decomp. 134°, and reacts in aqueous alcohol or acetone with 4-dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone and with hexamethylenetetramine to form salt-like compounds containing one mol. of each constituent; the former, $C_{27}H_{30}O_7N_4S$, forms crystals, decomp. 140—141°, and the latter, $C_{20}H_{25}O_6N_5S$, colourless needles, decomp. 167°.

Aqueous solutions of the alkali or alkaline earth salts of the ω-methylsulphonic acid of *p*-aminophenyl salicylate dissolve certain xanthine derivatives, such as caffeine and theophylline.

The *sodium ω-ethylsulphonate* of *p*-aminophenyl salicylate, colourless needles containing $1H_2O$, decomp. 149—150°, and the *sodium ω-propylsulphonate*, colourless plates, have been prepared.

C. S.

ω-Sulphonic Acids of *p*-Aminophenyl Salicylate and their Derivatives. II. J. ABELIN (*Annalen*, 1916, **411**, 229—244. Compare preceding abstract).—The stability of the ω-alkylsulphonic acids of *p*-aminophenyl salicylate decreases as the weight of the alkyl group increases; whilst the ω-methylsulphonic acid and its sodium salt are quite stable, the salts of the ω-ethyl- and -propylsulphonic acids are much less stable, and the alkali salts of the ω-amylsulphonic acid cannot be obtained pure. The stability is also diminished by substituents; the chloral bisulphite compound and *p*-aminophenyl salicylate do not yield a well-defined compound. Of the aromatic aldehyde bisulphite compounds, that of benzaldehyde reacts best with *p*-aminophenyl salicylate. Substitution in the phenyl group diminishes the stability of the ω-sulphonic acid. These differences in stability are probably related to the degree of hydrolytic dissociation of the aldehyde bisulphite compounds in aqueous solution.

Similar results have been obtained when *p*-aminophenol or *p*-phenetidine is used in place of *p*-aminophenyl salicylate.

The *sodium ω-methylsulphonate* of *p*-aminophenol,

$$OH\cdot C_6H_4\cdot NH\cdot CH_2\cdot O\cdot SO_2Na,H_2O,$$

colourless needles, is obtained by heating *p*-aminophenol and the formaldehyde bisulphite compound with water under quite definite conditions. The salt easily oxidises in acid solution, but does not darken in alkaline solution except after a considerable time. The free *acid* crystallises in leaflets.

p-Aminophenyl salicylate reacts with the bisulphite compounds of valeraldehyde and of chloral to form, not the expected ω-sulphonic acids, but with the former a *substance*, needles, decomp. 126—127°, and with the latter a non-halogenated *compound*, decomp. 155°.

An alcoholic suspension of *p*-aminophenyl salicylate reacts on the water-bath with an aqueous solution (or suspension) of benzaldehyde sodium hydrogen sulphite to form the *sodium ω-benzylsulphonate*, $OH\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot NH\cdot CHPh\cdot O\cdot SO_2Na,H_2O$, colour-

less needles, decomp. 117—119°, which in aqueous solution reduces ammoniacal silver oxide, but does not give a reddish-violet coloration with ferric chloride. The *sodium ω-benzylsulphonate* of *p*-phenetidine, $OEt\cdot C_6H_4\cdot NH\cdot CHPh\cdot O\cdot SO_2Na,H_2O$, crystals, decomp. 132—133°, is obtained in a similar way.

p-Aminophenyl *o*- and *m*-hydroxytoluates (but not the *p*-hydroxytoluate), by boiling with 5% alcoholic hydrogen chloride, yield *hydrochlorides*, $C_{14}H_{13}O_3N,HCl$, colourless needles, the former having decomp. 223—224°, darkening at 170°, and the latter decomp. 222°, reddening at about 180°.

The *sodium ω-methylsulphonates* of *p*-aminophenyl *o*- and *m*-hydroxytoluates, $OH\cdot C_6H_3Me\cdot CO\cdot O\cdot C_6H_4\cdot NH\cdot CH_2\cdot O\cdot SO_2Na,H_2O$, are prepared by the general method (preceding abstract); the former has decomp. 221—222° (free *acid*, crystals, with $1H_2O$, decomp. 134—136°), and the latter has decomp. 226—227° (free *acid*, needles, with $1H_2O$, decomp. 133—134°).

When equal molecular quantities of antipyrine and the ω-methylsulphonic acid of *p*-aminophenyl salicylate are warmed in water or aqueous alcohol, sulphur dioxide is evolved, and a *substance*, colourless needles, decomp. 149°, is obtained, which is proved to be a salt-like compound of *p*-aminophenyl salicylate and the ω-methylsulphonic acid of *p*-aminophenyl salicylate by its synthesis by heating these two components in aqueous alcohol. C. S.

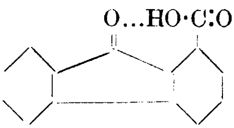
The Optical Anomaly of Fluorenone- and *allo*Chrysoketonecarboxylic Acids. A. HANTZSCH (*Ber.*, 1916, **49**, 226—232).—Notable colour differences exist between fluorenone-1-carboxylic acid (Goldschmiedt, A., 1903, i, 161; 1905, i, 132) and *allo*chrysoketone-1-carboxylic acid (Stobbe, A., 1907, i, 765) respectively, and their simple derivatives, such as the esters and salts; these derivatives are golden- to orange-yellow, whereas the free acids are red. At first sight these differences appear to be contradictory to the general result that the absorption of organic acids does not differ materially from that of their esters, and that although the salts may sometimes be rather more deeply coloured, they are never of a weaker colour; the facts therefore point to chromoisomerism.

In a recent investigation Stobbe (A., 1915, i, 542; compare Schaarschmidt, this vol., i, 47) decides from the absorption spectra of these acids in solution that there is no constitutional abnormality, but such a result throws no light on the peculiarly dark colour of the solid free acids.

All attempts to obtain isomeric forms of any of the derivatives of these acids proved fruitless, but as the yellow solutions of the free acids must contain in these compounds the ketonic configuration, the peculiar colour of the solid acids cannot be explained by the lactonic structure, because the lactonic form would be colourless.

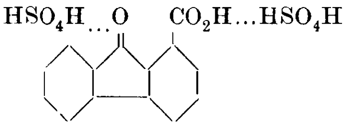
The fact that these acids contain a carbonyl and a carboxyl group in proximity to each other suggests that the abnormally deep colour may be due to intramolecular reaction between these

groups, probably with formation of an oxonium salt (formula annexed). This explanation meets all the facts. The solid acids have a colour resembling in depth that of the oxonium fluorenone nitrate, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>C{:}O\ .\ .\ .\ HNO_3$.



The isomeric fluorenone-4-carboxylic acid, in which the carbonyl and carboxyl groups are too widely apart for interaction, has a normal colour. Although the solutions of fluorenone-1-carboxylic acid in neutral solvents, such as alcohol or chloroform, resemble in colour the corresponding solutions of the esters, the solution in acetic acid has a distinctly deeper colour, whilst in trichloroacetic acid, fluorenone-1-carboxylic acid and *allo*chrysoketone-1-carboxylic acid possess the same colour as when in the solid state; the relation between the deep colour and the occurrence of an oxonium structure therefore appears incontrovertible.

When dissolved in sulphuric acid, these acids possess a still deeper colour, which is probably due to the formation of a dioxonium sulphate of the structure annexed. In accordance with this view, it is found that not only carbonyl compounds, but carboxyl compounds, such as benzoic acid and acetic acid, exist in solution in sulphuric acid as oxonium sulphates, the spectrum absorption being much stronger in this than in all other solvents (compare Hantzsch, A., 1908, ii, 14). D. F. T.



The Isomerism of the Benzil-*o*-carboxylic Acids and their Derivatives. A. HANTZSCH and A. SCHWIETE (*Ber.*, 1916, **49**, 213—226).—In extension of the investigation of the chromoisomerism of the colourless and yellow derivatives of dihydroxyterephthalic acid (Hantzsch, A., 1915, i, 551), the colourless and yellow forms of benzil-*o*-carboxylic acid and certain derivatives have been examined, with the result that chromoisomerism of a somewhat different type from the preceding has been recognised, to which the description "ketone-hydroxylactone isomerism" is applied.

The two modifications of benzil-*o*-carboxylic acid have already been described by Graebe (A., 1890, 989), as also have the yellow and colourless salts of benzildi-*o*-carboxylic acid and the yellow and colourless dialkyl esters; these colourless esters were regarded by Juillard (A., 1888, 955) and by Hönigsberger (*Annalen*, 1900, **311**, 266) as monoalkyl esters. Treatment with thionyl chloride converts the mono-acid into a colourless acid chloride, $C_{15}H_9O_3Cl$, m. p. 128°, whilst the action of phosphorus pentachloride on the acid in carbon disulphide solution yields a second colourless chloride, m. p. 61—63°, which can be converted into the isomeride by prolonged heating in chloroform solution. In some cases, also, coloured and colourless forms have been

observed with one salt of the monocarboxylic acid. There thus exist chromoisomeric forms of benzil-*o*-carboxylic acid, its salts, and esters, the yellow isomerides being of the ketonic structure $CRO\cdot CO\cdot C_6H_4\cdot CO_2X$, and the colourless compounds of the hydroxy-lactonic structure, $CO<\genfrac{}{}{0pt}{}{C_6H_4}{--O--}>C(OX)\cdot COR$, where X represents a hydrogen or metallic atom or an alkyl group, whilst R represents an aromatic radicle. The two colourless acid chlorides are also represented by the analogous formulæ $COCl\cdot C_6H_4\cdot CO\cdot COR$ and $CO<\genfrac{}{}{0pt}{}{C_6H_4}{--O--}>CCl\cdot COR$.

Of the dicarboxylic acids and their derivatives, only the diketonic and the dilactonic forms are known.

The close similarity between the isomerism of the benzil-*o*-carboxylic acids and that of the *o*-benzoylbenzoic acids is demonstrated by optical examination. The ketonic esters of *o*-benzoylbenzoic acid, the corresponding salts, and the free acid itself exhibit spectrum absorption similar to that of benzophenone, whereas the esters of hydroxylactonic structure give an absorption curve of a different type. Similarly, the yellow series of esters derived from the mono- and di-carboxylic acids of benzil prove their ketonic structure by the close resemblance of their absorption curves to that of benzil, whilst the lactonic ester has a quite distinct type of curve, but very like that of the lactonic esters of *o*-benzoylbenzoic acid; hence also the yellow free acids and the yellow salts are ketonic derivatives, whilst the colourless form of the monocarboxylic acid and the colourless salts are hydroxy-lactone derivatives. It is noteworthy that whereas the chromoisomeric derivatives of benzil optically are quite different, the colourless and yellow chromoisomerides among the dihydroxyterephthalic acid compounds optically are closely alike, the chief difference lying merely in the position of the absorption curve, this peculiarity being due to the latter isomerism depending on the relatively slight change

$$\cdot C(OH)\colon CH\cdot CO_2R \text{ to } \cdot CO\cdot CH\colon C(OH)\cdot OR.$$

The most definite confirmation of the hydroxylactone–ketone nature of the isomerism of the benzil-*o*-carboxylic acid derivatives is observable with the two colourless chlorides of benzildi-*o*-carboxylic acid, one of which, m. p. 194—196°, reacts with water and alcohols in the manner of a true acid chloride, and therefore possesses the constitution $COCl\cdot C_6H_4\cdot CO\cdot CO\cdot C_6H_4\cdot COCl$; the other, m. p. 250—253°, can be recrystallised unaltered from alcohol, and from its identity with the product of the addition of chlorine to diphthalyl must be regarded as of the structure

$$C\ O<\genfrac{}{}{0pt}{}{C_6H_4}{--O--}>CCl\cdot CCl<\genfrac{}{}{0pt}{}{C_6H_4}{--O--}>CO.$$

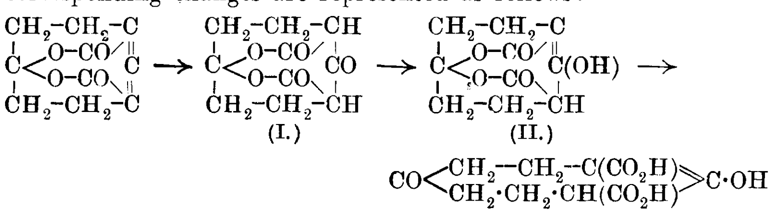
The yellow salts also indicate their ketonic structure by retaining their colour in alkaline solution, whereas lactones and hydroxylactones undergo fission on treatment with alkali.

Unlike the case of benzil-*o*-monocarboxylic acid, only one form of the dicarboxylic acid is known, but chromoisomerism is observable with the salts of each, some being coloured whilst others are

colourless, and occasionally the salt with one metal being obtainable in a coloured and a colourless form.

The conditions under which transformation can occur from one series to the other are discussed, the chief agent of change being alteration in temperature. The isomeric esters and chlorides dissolve unaltered in inactive solvents, but the colourless salts of the mono- and di-carboxylic acids dissolve, giving yellow solutions optically identical with those derived from the yellow salts. With the free benzilmono-*o*-carboxylic acid the absorption of the alcoholic solution indicates an equilibrium between the two forms, the ketonic form, however, largely preponderating. D. F. T.

Anemonin. Y. Asahina (*Arch. Pharm.*, 1915, **253**, 590—603. Compare A., 1914, i, 561; 1915, i, 1067).—In agreement with the statement of Beckurts (A., 1892, 1241), and contrary to that of Meyer (A., 1896, i, 623; 1899, i, 930), the author finds that towards bromine or hydrogen bromide, anemonin behaves like a diolefine, the tetrabromide, $C_{10}H_8O_4Br_4$, having, however, m. p. 175° (undecomp.). Anemoninic acid, formed by hydrolysis of anemonin with combination of two mols. of water, has now been obtained crystalline in the form of stellate groups of white, hygroscopic needles, m. p. 116—117° (compare Beckurts, *loc. cit.*). The relation between anemonic and anemoninic acids does not appear to be so simple as was indicated by Beckurts, since the characteristic colour reaction of the latter with alkali is not shown by the former. When anemonin is heated with the exactly equivalent proportion of alkali hydroxide solution, a transitory, reddish-brown coloration, rapidly changing to the pale yellow of the neutral anemoninate, is observed; subsequent addition of a few drops of the alkali solution restores the reddish-brown coloration. The corresponding changes are represented as follows:



(I.) (II.) (III.)

Compound I, first formed, contains a methine group lying between two carbonyl groups, and has therefore a reactive hydrogen atom. The temporary reddish-brown coloration is due to compound II, which forms a coloured anhydride salt. The pale yellow, neutral salt of anemoninic acid (III) is converted by alkali into a reddish-brown enolic salt (compare Stobbe, A., 1908, i, 985; Dieckmann, A., 1914, i, 691). Catalytic reduction of anemoninic acid results in the absorption of one mol. of hydrogen and formation of anemonolic acid, whereas anemonic acid readily absorbs two mols. Hydrolysis of anemonin by means of sodium ethoxide and purification of the acid thus obtained by way of its lead salt yields

α-anemonic acid, m. p. 120°, which is converted into the β-isomeride, m. p. 210° (compare Beckurts, *loc. cit.*; Meyer, *loc. cit.*), by boiling with dilute hydrochloric acid. On the assumption that formula III correctly represents anemoninic acid, the constitution of anemonolic acid would be $CO<\begin{matrix}CH_2\cdot CH_2\cdot CH(CO_2H)\\CH_2\cdot CH_2\cdot CH(CO_2H)\end{matrix}>CH\cdot OH$ (compare Meyer, *loc. cit.*).

Anemonin dihydrobromide, $C_{10}H_8O_4,2HBr$, forms fine, felted needles, m. p. 182° (efferves.).

α-Anemonic acid, $C_{10}H_{10}O_5$, forms stellate groups of white needles; its *sodium*, *potassium*, and *lead* salts, and its *semicarbazone*, $C_{11}H_{13}O_5N_3,\frac{1}{2}H_2O$, m. p. 220°, and *phenylhydrazone*, m. p. 235° (efferves.), were prepared.

β-Anemonic acid forms a *semicarbazone*, charring without melting at about 270°, and a *phenylhydrazone*, which begins to melt at about 220° and decomposes with effervescence at 245°.

The compound, $C_{18}H_{20}O_4N_2$, obtained by the action of phenylhydrazine on dimethylanemonin, forms slender, deep yellow needles, m. p. 180°; Meyer (*loc. cit.*) gave m. p. 170°.

Anemonolic acid yields a sparingly soluble *semicarbazone*, $C_{14}H_{24}O_8N_6$, in the form of a white, crystalline precipitate, m. p. 185° (decomp.). T. H. P.

Mellitic Acid and its Nitrogenous Derivatives. OTTO MUMM (*Annalen*, 1916, **411**, 244—272).—The identity of the trimethylparamide synthesised from triketo-3-acetyl-1-methylpyrrolidine (acetylhydroxymaleinmethylimide) by Mumm and Bergell (A., 1912, i, 1015) with that obtained from mellitic acid and methylamine by Meyer and Steiner (A., 1914, i, 963) has been proved by a comparison of their crystalline forms and of the course of their hydrolysis by aqueous sodium hydroxide.

A by-product, which is soluble in water, obtained in the preparation of trimethylparamide from mellitic acid and methylamine by a slight modification of Meyer and Steiner's method, is *dimethyleuchroic acid*, $C_{14}H_8O_8N_2$, colourless, rhomic plates with $2H_2O$, which responds to the euchrone reaction, and probably has the constitution $NMe<\begin{matrix}CO\cdot C\cdot C(CO_2H):C\cdot CO\\ \quad\ \ \| \qquad\qquad\quad\ \ | \\CO\cdot C\cdot C(CO_2H):C\cdot CO\end{matrix}>NMe$, since it cannot be converted into trimethylparamide by heating the methylammonium salt at 200°. Since the acid crystallises even from alcohol with $2H_2O$, the possibility exists that it is a dimethylamide of mellitic acid, $C_6(CO_2H)_4(CO\cdot NHMe)_2$, but this is disproved by the fact that the acid behaves as a dibasic acid towards sodium hydroxide; the dimethylamide (or dimethylammonium salt) is produced, however, when the acid is digested for a long time with an excess of the alkali.

The response of dimethyleuchroic acid to the euchrone reaction (reduction with zinc) shows that the formation of the coloured (blue or violet) product cannot be due to a tautomeric change (in the case of euchroic acid itself) of $NH<\begin{matrix}CO\cdot\\CO\cdot\end{matrix}$ to $N\leqslant\begin{matrix}CO\\C(OH)\cdot\end{matrix}$, since

such a change is impossible in the case of dimethyleuchroic acid; possibly a quinonoid compound, such as

$$NMe<\begin{matrix}CO\text{---}C\text{:}C(CO_2H)\cdot C\text{:}C(OH)\\ C(OH)\text{:}C\cdot C(CO_2H)\text{:}C\text{---}CO\end{matrix}>NMe,$$

is formed.

Ammonium mellitate has been heated under various conditions, at the ordinary pressure or in a vacuum, at temperatures from 160—195°, for periods varying from a few to ten hours, and always in a slow current of air; the product in all cases is essentially the same, consisting of a mixture of euchroic acid and paramide. In only a few of the experiments has the euchroic acid obtained given analytical results corresponding with the formula $C_{24}H_9O_{15}N_5$ (Meyer and Steiner, *loc. cit.*); in most cases its composition differed from this and also from the formula $C_{12}H_4O_8N_2$ found by Wöhler in 1841.

Paramide resembles trimethylparamide in its behaviour during titration with alkali and in losing only two molecules of ammonia easily by distillation with aqueous sodium hydroxide, but differs from it in that by treatment with a slight excess of very dilute aqueous sodium hydroxide at 0°, followed as quickly as possible by acidification, it yields a colourless, amorphous, occasionally microcrystalline, substance which contains $\frac{1}{2}H_2O$ more than paramide, and has the composition $C_{24}H_8O_{13}N_6$.

The examination of the crude euchroic acid obtained above shows that three euchroic acids occur, namely, *euchroic acid* (*a*), $C_{12}H_4O_8N_2$ (corresponding with Wöhler's formula), *euchroic acid* (*b*), $C_{24}H_9O_{15}N_5$ (corresponding with Meyer and Steiner's formula), and *euchroic acid* (*c*), $C_{48}H_{17}O_{31}N_9$. The last behaves as an octabasic acid when titrated with sodium hydroxide (and phenolphthalein as indicator) in the cold, but after complete hydrolysis 15 mols. of the alkali are neutralised. The conditions for the production of the (*b*) acid cannot be stated with certainty, but the (*a*) acid is obtained by vigorously boiling for twenty minutes a solution of euchroic acid (*c*) in the exact quantity of 2*N*-hydrochloric acid required to dissolve it; on cooling, the (*a*) acid crystallises in colourless plates.

The three acids differ in their nitrogen content; in their other properties scarcely any differences are to be detected. Constitutional formulæ based on that of dimethyleuchroic acid are suggested. C. S.

The Chromoisomerism of the Salts of Phenol-aldehydes. A. HANTZSCH (*Ber.*, 1916, **49**, 234—236).—A reply to Pauly (A., 1915, i, 689) criticising several of the latter's statements.

D. F. T.

Conversion of ψ-Ionone into Ionone. G. SCHULTZ and E. GÖTTELMANN (D.R.-P., 288688; from *J. Soc. Chem. Ind.*, 1916, **35**, 437).—ψ-Ionone is converted into ionone by prolonged heating at 150—180° with acetic, propionic, butyric, or benzoic acid. By repeated treatment of the fraction of higher boiling point containing unchanged ψ-ionone, a yield of 70% can be obtained. G. F. M.

The Addition of Aliphatic Nitro-compounds to Unsaturated Compounds. E. P. KOHLER (*J. Amer. Chem. Soc.*, 1916, **38**, 889—900).—The object of the work was to find a method of preparing *cyclo*propane derivatives having a nitro-group attached to one of the ring carbon atoms. Sodium nitromethane readily combines with phenyl styryl ketone to give the sodium derivative of γ-nitro-β-phenylbutyrophenone, $NO_2\cdot CH_2\cdot CHPh\cdot CH_2\cdot COPh$. When bromine is added to the nitro-ketone itself, it gives a pair of α-monobromo-derivatives, from which sodium ethoxide rapidly removes hydrogen bromide, giving a nitro*cyclo*propane. The sodium derivative on bromination gives sodium bromide and two isomeric γ-monobromo-derivatives, which on reduction only yield the nitro-ketone. Other nitro-paraffins, both primary and secondary, can be used in place of nitromethane. The nitro-esters may even be used, but give a mixture of products unless the nitro-compound is secondary, when the sole product is a lactone, which, when digested with hydrochloric acid, passes into the required nitro-ketone. The only unsaturated compound used in this work was phenyl styryl ketone, but the work is being extended to others.

Nitromethane and phenyl styryl ketone only react in the presence of a condensing agent, the most satisfactory being sodium methoxide, an excess of nitromethane being used. The sodium methoxide in methyl alcohol solution is added, with constant shaking, to a solution of phenyl styryl ketone and nitromethane in the same solvent at about 40°. The yellow liquid is cooled and acidified with glacial acetic acid. The whole is cooled in a freezing mixture, and the nitro-ketone is collected. γ-*Nitro-β-phenylbutyrophenone*, $NO_2\cdot CH_2\cdot CHPh\cdot CH_2\cdot COPh$, crystallises in thin, white needles, m. p. 103°, and gives a *semicarbazone*, plates, m. p. 165°; it does not reduce potassium permanganate when in acetone solution. On adding sodium to its benzene solution and heating, *sodium* aci-*nitrophenylbutyrophenone* is readily obtained as a microcrystalline powder, and is quickly hydrolysed in aqueous solution. The dry sodium derivative when added gradually to bromine dissolved in chloroform gives a mixture of two isomeric γ-*bromo-γ-nitro-β-phenylbutyrophenones*, $NO_2\cdot CHBr\cdot CHPh\cdot CH_2\cdot COPh$, one crystallising in needles, m. p. 90°, the other in thin plates, m. p. 93°. Both these bromo-derivatives readily dissolve in sodium methoxide and unite with bromine, giving $\gamma\gamma$-*dibromo-γ-nitro-β-phenylbutyrophenone*, m. p. 160—162°. These γ-bromo-derivatives are readily reduced when boiled in alcohol or acetone solution with potassium iodide or potassium cyanide, giving the original nitro-ketone.

When nitrophenylbutyrophenone is brominated in chloroform, the bromine enters in the α-position, the chief product being α-*bromo-γ-nitro-β-phenylbutyrophenone*,

$$NO_2\cdot CH_2\cdot CHPh\cdot CHBr\cdot COPh,$$

colourless needles, m. p. 100°, together with a small amount of an *isomeride*, m. p. 86°, and a little of a *dibromo*-derivative, prisms, m. p. 105°. When slightly more than one equivalent of potassium iodide is added to each of the α-bromo-compounds dissolved in the

smallest quantity of boiling methyl alcohol, the same *α-iodo-γ-nitro-β-phenylbutyrophenone*, pale yellow needles, m. p. 123°, is obtained. The α-halogen compounds readily lose the hydrogen haloid when treated with sodium ethoxide, potassium acetate, or potassium cyanide, giving the same cyclo*propane* derivative, m. p. 93°. The γ-bromo-compounds can be further brominated in chloroform solution, giving αγ-bromo-compounds. The following were prepared: *αγ-dibromo-γ-nitro-β-phenylbutyrophenone*, needles, m. p. 130°, which when boiled with potassium iodide in alcoholic solution gave the α-iodo-compound, m. p. 123° (see above), and when boiled in alcoholic solution with zinc dust gave a very poor yield of the *cyclo*propane derivative, m. p. 93°.

A similar series of compounds has been obtained using nitroethane in place of nitromethane.

γ-Nitro-β-phenylvalerophenone,

$$NO_2\cdot CHMe\cdot CHPh\cdot CH_2\cdot COPh,$$

was obtained as two stereoisomerides, one crystallising in fine needles, m. p. 72°, and the other in stout needles or plates, m. p. 100°.

γ-Bromo-γ-nitro-β-phenylvalerophenone,

$$NO_2\cdot CMeBr\cdot CHPh\cdot CH_2\cdot COPh,$$

crystallises in fine needles, m. p. 17°, a second product, m. p. 160°, being obtained during its preparation.

α-Bromo-γ-nitro-β-phenylvalerophenone,

$$NO_2\cdot CHMe\cdot CHPh\cdot CHBr\cdot COPh,$$

was not isolated as such, but two solid *cyclo*propane derivatives were obtained from it.

β-Nitropropane under slightly modified conditions similarly yielded *γ-nitro-β-phenyl-γ-methylvalerophenone*,

$$NO_2\cdot CMe_2\cdot CHPh\cdot CH_2\cdot COPh,$$

m. p. 167°, which showed no tendency to form metallic derivatives. *α-Bromo-γ-nitro-β-phenyl-γ-methylvalerophenone*,

$$NO_2\cdot CMe_2\cdot CHPh\cdot CHBr\cdot COPh,$$

was obtained in two isomeric forms, one crystallising in diamond-shaped plates, m. p. 165°, and the other in stout prisms, m. p. 125°.

W. G.

Hylotropic Isomeric Modifications of Substances. KARL SCHAUM, KARL SCHAELING, and FRIEDRICH KLAUSING (*Annalen*, 1916, **411**, 161—195).—When about 2 c.c. of fused α-benzophenone are heated at 220° for about forty-five minutes and cooled slowly to the ordinary temperature, and finally in ether–carbon dioxide, about 80% of the product is obtained in the form of very stable crystals of the metastable β-benzophenone; these are almost unaffected by pressure or friction, and can be kept unchanged for a year or longer. To achieve a successful result, scrupulous cleanliness of the hands and vessels is essential, and "spores" of the α-modification must be entirely absent.

Comparative determinations of the physical constants of α- and β-benzophenones in the fused state and in solution have been made; the refractive indices and the viscosities of the fused

substances and the ultraviolet absorption spectra of solutions (but not of the fused substances) show small but appreciable differences (compare Schaum, A., 1910, i, 391). The two modifications of benzophenone, therefore, when freshly fused or dissolved, must be chemically isomeric, and the "polymorphism" of benzophenone must be a case of equilibrium isomerism.

The freezing points of the fused β-modification to which varying quantities of α-crystals have been added, and, conversely, of the fused α-modification to which the β-modification has been added (the latter must be added in the fused state, since the observation has been made that β-crystals are converted into α-crystals in contact with the fused α-modification), have been determined. Whilst in the latter case the freezing point remains almost constant, the freezing point of the β-modification in the former varies considerably (several tenths of a degree) with the amount of α-form added. The conclusion is drawn that the β-crystals are mixed crystals, and the stability of this metastable modification increases as the proportion of the α-molecules therein diminishes.

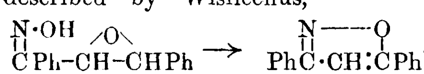
By passing hydrogen chloride through the fused α-modification at 48°, it is shown that the conversion of the α- into the β-modification can be catalytically accelerated.

Experiments analogous to the preceding, and with similar results, have been conducted with α- and β-phenyl *p*-tolyl ketones.

Five hundred and fifty organic substances have been examined by the aid of Lehmann's polarisation microscope, and of the 80 cases which proved to be polymorphous, 57 have not hitherto been recorded in the literature; these are tabulated, their degree of polymorphism and enantiotropy or monotropy being stated.

C. S.

Benzoylphenylethylene Oxide, a Third Isomeride of Dibenzoylmethane. Oskar Widman (*Ber.*, 1916, **49**, 477—485).—The properties of α-benzoyl-β-phenylethylene oxide (A., 1913, i, 1220) have been more completely investigated. It readily reacts with hydrogen chloride, and yields with hydroxylamine, semicarbazide, and hydrazine previously unknown substances which, by rupture of the oxide ring, pass into derivatives of the 1:3-diketone described by Wislicenus,



A somewhat different change occurs with alcoholic alkali, a 1:2-diketone being first formed and then converted into a hydroxy-carboxylic acid in accordance with the scheme

$$\mathrm{COPh{\cdot}\overbrace{CH{-}CHPh}^{O} \longrightarrow COPh{\cdot}CO{\cdot}CH_2Ph \longrightarrow CH_2Ph{\cdot}CPh(OH){\cdot}CO_2H.}$$

Benzoylphenylethylene oxide chlorohydrin, m. p. 106—107°, is prepared by the action of a cold, saturated solution of hydrogen chloride in alcohol on the oxide.

Under varying conditions, benzoylphenylethylene oxide yields a number of oximes, the configurations of which have not been

determined. When an alcoholic solution of the oxide is treated at the ordinary temperature with a concentrated aqueous solution of hydroxylamine hydrochloride, the *α-oxime*, long needles, m. p. 169—169·5°, separates; with hydroxylamine, on the other hand, the *β-oxime*, needles, m. p. 161°, is obtained, together with a mixture of γ- and δ (?)-*oximes*, which were not separated; these are readily converted by hydrogen chloride into the α-oxime. The α-oxime and the γ- and δ-mixture are readily converted by concentrated sulphuric acid in glacial acetic acid solution into diphenyl*iso*oxazole, m. p. 141°.

Phenylhydrazine converts the oxide into 2:3:5-triphenylpyrazole, m. p. 138—138·5°, a phenylhydrazone with intact oxide group not being isolated.

The *hydrazone* of *benzoylphenylethylene oxide*, colourless needles, m. p. 209°, is obtained by the action of hydrazine hydrate on a warm alcoholic solution of the oxide. The *hydrochloride*, fine, white needles, *platinichloride*, yellow, crystalline powder, and *acetyl* derivative, m. p. 139—140°, are described. Excess of boiling sodium ethoxide solution converts the hydrazone into diphenylpyrazole, m. p. 199° (*acetyl* derivative, six-sided leaflets, m. p. 87°).

The *semicarbazone* of *benzoylphenylethylene oxide* forms six-sided prisms, which have m. p. 150—158°, then resolidify and again melt at 183—184° (decomp.). When cautiously heated to its m. p., diphenylpyrazole, m. p. 199°, is formed with explosive violence.

When an alcoholic solution of the oxide is boiled for a short time with sodium ethoxide, a yellow oil is formed, the investigation of which is not complete, but which doubtless contains phenylbenzylglyoxal, $COPh\cdot CO\cdot CH_2Ph$, together with its enolic form, since it is converted by *o*-phenylenediamine into 2-*phenyl*-3-*benzylquinoxaline*, colourless prisms, m. p. 98—99°. Protracted boiling with alcoholic sodium ethoxide solution causes the conversion of the oxide into phenylbenzylglycollic acid, needles, m. p. 165—166°. The latter is oxidised by potassium dichromate to deoxybenzoin. H. W.

Certain Derivatives of Tetrabromo-*o*-benzoquinone. C. Loring Jackson and Sydney A. Beggs (*J. Amer. Chem. Soc.*, 1916, **38**, 676—685).—The actions of potassium sulphite and dimethylamine on tetrabromo-*o*-benzoquinone are described.

When a benzene solution of the quinone is shaken with an aqueous solution of potassium sulphite in the cold, the red colour gradually disappears and *potassium dibromocatecholdisulphonate*, $C_6Br_2(OH)_2(SO_3K)_2$, separates in clusters of white needles, which reduce silver nitrate, give a deep blue colour with ferric chloride, and are converted into potassium euthiochronate on boiling with potassium hydroxide. The *barium* salt, $3H_2O$, and the *calcium* salt, $4H_2O$, are white, crystalline substances. The potassium salt was oxidised by rubbing with concentrated nitric acid to potassium dibromo-*o*-benzoquinonedisulphonate, but this could not be freed

from a trace of potassium nitrate. Anodic oxidation was therefore tried, but the process could not be stopped at the desired stage, the ultimate product being pentabromoacetone.

Using warm solutions of tetrabromo-*o*-benzoquinone and potassium sulphite, the authors occasionally obtained a *compound* which they believe has the constitution $[(OH)_2C_6(SO_3K)_5]_2O,H_2O$. It crystallises in white plates.

The action of secondary amines on tetrabromo-*o*-benzoquinone gave disappointing results in view of the fact that aniline gave well-defined derivatives (A., 1903, i, 102). Dimethylamine gave unstable, black crystals of a *compound*, $C_6O_2Br_4(NHMe_2)_2$, decomp. 115—125°. J. C. W.

Reduction Products of 1- and 2-Benzoylanthraquinones. ALFRED SCHAARSCHMIDT and D. IRINEU (*Ber.*, 1916, **49**, 386—396. Compare A., 1915, i, 566, 696).—The reduction of 1- and 2-benzoylanthraquinones in acid and alkaline media has been more thoroughly investigated. The following reactions are now recognised. The 1-benzoylanthraquinones yield blue pinacone derivatives when reduced in acid solution, but are only slightly attacked in ammoniacal solutions, whilst the 2-benzoylanthraquinones give benzoylanthranols in acid media and anthracylphenylcarbinols in ammoniacal solutions.

A mixture of 2-*p*-toluoylanthraquinone and aluminium powder (equivalent to 6H) was added to an excess of concentrated sulphuric acid, and the reduction product, after pouring on ice, washing and drying, was boiled with acetic anhydride and sodium acetate, when 2-p-*toluoylanthran*-10-*ol acetate*,

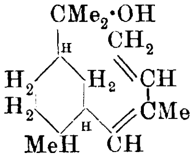
$$C_6H_4<\begin{matrix}CH\text{——}\\ |\\ C(OAc)\end{matrix}>C_6H_3\cdot CO\cdot C_6H_4Me,$$

was obtained in pale greenish-yellow crystals, m. p. 154—154·5°. Reduction with zinc dust and 20% ammonia solution at 70—80° yielded a product which was crystallised several times from glacial acetic acid, and then obtained in very pale yellow crystals, m. p. 164—165°. The substance was considered to be 2-*anthracyl*-p-*tolylmethyl acetate*, $C_6H_4<\begin{matrix}CH\\ |\\ CH\end{matrix}>C_6H_3\cdot CH(OAc)\cdot C_6H_4Me$.

1-*p*-Chlorobenzoylanthraquinone yielded a small amount of the same blue pinacone derivative when reduced by zinc and ammonia as is the chief product of the reduction by aluminium and concentrated sulphuric acid (*ibid.*). J. C. W.

Zingiberol. A New Sesquiterpene Alcohol Occurring in the Essential Oil of Ginger. BENJAMIN T. BROOKS (*J. Amer. Chem. Soc.*, 1916, **38**, 430—432).—A fraction of ginger oil, free from terpenes and sesquiterpenes, with b. p. 154—157°/14·5 mm., is found to possess the fragrance of ginger and to be the alcohol related to zingiberene. It is therefore designated *zingiberol*, and, assuming the correctness of Semmler's formulæ for zingiberene and

*iso*zingiberene (A., 1913, i, 742), it would have either of the annexed formulæ.



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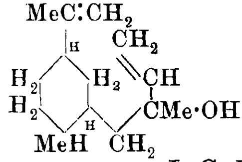


J. C. W.

Derivatives of Methylenecamphor. HANS RUPE and MARTIN ISELIN (*Ber.*, 1916, **49**, 25—50).—On account of the presence of the conjugation of the ethylenic and ketonic linkings in derivatives of methylenecamphor of the type $C_8H_{14}<\begin{matrix}C:CHR\\ |\\ CO\end{matrix}$, these substances supply attractive material for an investigation of the influence of constitution on the rotatory power of optically active compounds. Few compounds of this class have hitherto been prepared (Bishop, Claisen, and Sinclair, A., 1895, i, 62; Haller, A., 1903, i, 503, 563; Haller and Bauer, A., 1906, i, 441; Haller and Minguin, A., 1903, i, 267; Minguin, A., 1903, i, 428; 1904, i, 330; Haller and March, A., 1906, i, 296). The authors have discovered a convenient general method for the preparation of such substances by the reaction of chloromethylenecamphor,

$$C_8H_{14}<\begin{matrix}C:CHCl\\ |\\ CO\end{matrix}$$

with various organo-magnesium compounds; the reaction occurs more smoothly with the magnesium aryl haloids than with the alkyl compounds. The correctness of the view as to the constitution of the products was confirmed by the identity of benzylidene and *cyclo*hexylmethylene derivatives with these substances as produced by other methods, and also by the behaviour of a typical alkylidene and arylidene derivative towards ozone.

Chloromethylenecamphor can be conveniently prepared by the action of thionyl chloride on hydroxymethylenecamphor, the product being a colourless oil, b. p. 113°/12·5 mm., $[\alpha]_D^{20}$ +180·28° (in benzene); the reaction is endothermic to the extent of 118 cal. for the formation of 5·22 grams of chloro-compound; the chloro-compound forms a crystalline *additive compound* with hydrogen bromide.

When treated with magnesium methyl bromide in ethereal solution, chloromethylenecamphor is converted into ethylidenecamphor, $C_8H_{14}<\begin{matrix}C:CHMe\\ |\\ CO\end{matrix}$, radiate crystals, m. p. 28—29°, b. p. 109—110°/12 mm., $[\alpha]_D^{20}$ +178·58° (in benzene). This substance has already been described (Haller and Minguin, *loc. cit.*) as a liquid, $[\alpha]_D$ +113° (in alcohol), which appears to suggest that the earlier product was not optically pure, although the possibility of isomerism is not excluded.

Propylidenecamphor, $C_8H_{14}<\begin{matrix}C:CHEt \\ | \\ CO\end{matrix}$, prepared in a similar manner to the preceding, but with the use of magnesium ethyl bromide, is a colourless, aromatic oil, b. p. 121—122°/13 mm., D_4^{20} 0·9448, $[\alpha]_D^{20}$ +172·95° in substance, +171·26° in alcohol, and +157·44° in benzene.

n-*Butylidenecamphor*, $C_8H_{14}<\begin{matrix}C:CHPr \\ | \\ CO\end{matrix}$, prepared by the general method, is a colourless, aromatic liquid, b. p. 131—132°/12 mm., D_4^{20} 0·9380, $[\alpha]_D^{20}$ +161·95° in substance, +149·32° in benzene.

iso*Amylidenecamphor*, $CHMe_2\cdot CH_2\cdot CH:C<\begin{matrix}C_8H_{14} \\ | \\ CO\end{matrix}$, obtained by the general procedure, is a fairly liquid, aromatic oil, b. p. 136—138°/12 mm., D_4^{20} 0·9275, $[\alpha]_D^{20}$ +156·59° in substance, +145·04° in benzene. When treated in carbon tetrachloride solution with ozone, this substance yielded camphorquinone, camphoric acid, and *iso*valeric acid.

In all these cases the primary product from the Grignard reaction was contaminated with unaltered chloromethylenecamphor, which was generally removed by treatment with alcoholic potassium hydroxide. However, with magnesium allyl bromide the resulting product was still less pure, and consisted of an oil, which decomposed with evolution of a gas when distilled under reduced pressure, and finally, after treatment with alcoholic potassium hydroxide, a mobile *hydrocarbon*, $C_{10}H_{14}$ or $C_{10}H_{12}$, was obtained, b. p. 107—108°/13 mm., with an odour recalling that of borneol.

Benzylidenecamphor, $C_8H_{14}<\begin{matrix}C:CHPh \\ | \\ CO\end{matrix}$, obtained by the general method, was a colourless, crystalline solid, m. p. 98·5°, $[\alpha]_D^{20}$ +426·55° in benzene, whereas Haller found +425·1° in toluene.

Phenylethylidenecamphor, $C_8H_{14}<\begin{matrix}C:CH\cdot CH_2Ph \\ | \\ CO\end{matrix}$, was obtained as an oil of very faint greenish-yellow colour, b. p. 199—202°/12 mm., 124—126°/0·1 mm., D_4^{20} 1·0250, $[\alpha]_D^{20}$ +129·00° in substance, +115·72° in benzene, +129·83° in alcohol, which was accompanied by a mobile, colourless, almost inodorous *substance*, $C_{12}H_{14}O$, b. p. 143—144·5°/14 mm. When submitted to ozonisation, with subsequent treatment with water, phenylethylidenecamphor gave camphorquinone and camphoric acid with a little phenylacetic acid, the small yield of the last being due to the destructive action of ozone on this acid.

Phenylpropylidenecamphor, $CH_2Ph\cdot CH_2\cdot CH:C<\begin{matrix}C_8H_{14} \\ | \\ CO\end{matrix}$, was obtained as a viscid, pale yellow, inodorous oil, b. p. 208—210°/13·5 mm., 152—154°/0·1 mm., D_4^{20} 1·0094, $[\alpha]_D^{20}$ +127·99° in substance, +117·70° in benzene.

Phenylbutylidenecamphor, $CH_2Ph \cdot CH_2 \cdot CH_2 \cdot CH{:}C<\begin{matrix}C_8H_{14}\\ | \\ CO\end{matrix}$, prepared with the use of magnesium phenylethyl bromide, was a pale yellow, viscous, inodorous oil, b. p. 221—223°/15 mm., D_4^{20} 0·9990, $[\alpha]_D^{20}$ +113·33° in substance, +108·03° in benzene.

*cyclo*Hexylmethylenecamphor, $C_8H_{14}<\begin{matrix}C{:}CH \cdot C_6H_{11}\\ | \\ CO\end{matrix}$, prepared with the use of magnesium *cyclo*hexyl bromide, was obtained as colourless prisms, m. p. 46—48° (compare Haller, *loc. cit.*).

a-Naphthylidenecamphor, $C_8H_{14}<\begin{matrix}C{:}CH \cdot C_{10}H_7\\ | \\ CO\end{matrix}$, was obtained in long, transparent prisms, m. p. 98—99·5°, b. p. 253—254°/12·5 mm., $[\alpha]_D^{20}$ +353·62° in benzene, with slight mutarotation.

Endeavours were made to prepare a diphenyl derivative of methylenecamphor, but the action of magnesium on a solution of iododiphenyl and chloromethylenecamphor in a mixture of benzene and ether yielded much diphenyl with smaller quantities of bidiphenyl, $C_6H_4Ph \cdot C_6H_4Ph$, and *substances*, m. p. 183—184°, 280—281°, and 138—143° respectively. Attempts to induce the interaction of diphenylbromomethane and chloromethylenecamphor produced tetraphenylethane. The action of magnesium on chloromethylenecamphor in ethereal solution gave a *substance*, $C_{10}H_{14}O$, m. p. 254—256°, whilst with a mixture of ether and benzene as solvent the product consisted of a mixture of *substances*, colourless needles, m. p. 183—184°, and yellow prisms, m. p. 280—281°, a similar mixture to this having been obtained as a by-product in the preparation of ethylidenecamphor.

Several of the above derivatives of methylenecamphor were submitted to reduction with sodium amalgam in methyl-alcoholic solution, which was maintained neutral by the addition of 50% acetic acid. The following substances were obtained in this way: iso*Amylcamphor*, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CH<\begin{matrix}C_8H_{14}\\ | \\ CO\end{matrix}$, a colourless, inodorous, fairly mobile oil, b. p. 140°/14 mm., D_4^{20} 0·9197 $[\alpha]_D^{20}$ +66·78° in substance, +42·34° in benzene. *Phenylethylcamphor*, $CH_2Ph \cdot CH_2 \cdot CH<\begin{matrix}C_8H_{14}\\ | \\ CO\end{matrix}$, colourless prisms, m. p. 60—61°, to a viscous oil, b. p. 201—202°/15 mm., $[\alpha]_D^{20}$ +22·82° in benzene, which was accompanied by a *substance*, b. p. 308—310°/11 mm., possibly a pinacone. Phenylpropylcamphor,

$$CH_2Ph \cdot CH_2 \cdot CH_2 \cdot CH<\begin{matrix}C_8H_{14}\\ | \\ CO\end{matrix},$$

a colourless oil, b. p. 208—210°/15 mm., $[\alpha]_D^{20}$ +52·37° in benzene; a substance of this composition has also been described by Rupe and Frisell (A., 1905, i, 220, 362).

In the case of all the compounds described above, the optical activity was measured for various wave-lengths, and the observed specific exaltation for the methylene derivatives is in accord with

that expected for a disturbed conjugation, the disturbing influence in this group of compounds being due to the camphor nucleus.

D. F. T.

Japanese Oil of Pepper. Xanthoxylin. H. THOMS (*Chem. Zentr.*, 1915, ii, 1186—1187; from *Arbeit. Pharm. Inst. Univ. Berlin*, 1914, **11**, 58—59).—Xanthoxylin (phloracetophenone dimethyl ether) is present in the oils derived from *Xanthoxylum alatum* and *X. aubertia*, but not in the true Japanese oil of pepper obtained from *X. piperitum*. The yield of the last-named oil was 4·33%, calculated on the weight of the fruits taken (see next abstract).

D. F. T.

Japanese Oil of Pepper (from Xanthoxylum piperitum, D.C.). M. DURUTTIS (*Chem. Zentr.*, 1915, ii, 1187; from *Arbeit. Pharm. Inst. Univ. Berlin*, 1914, **11**, 60—63. Compare preceding abstract).—The oil had D^{20} 0·890, n_D 1·47320, α_D +26·5. By fractional distillation the liquid was separated into several portions; the most volatile part, b. p. 175—178°, appeared to consist chiefly of dipentene and α-limonene. In the less volatile portions, palmitic acid and combined acetic acid were present, indications of cuminaldehyde and esterified geraniol also being observed. Methyl cinnamate was not present.

D. F. T.

Croton-resin. R. BOEHM (*Arch. Pharm.*, 1915, **253**, 574—585. Compare Dunstan and Boole, A., 1895, i, 680).—In order to obtain pure croton-resin from crude croton oil, the latter is treated repeatedly in the cold with methyl alcohol, which dissolves the resin, the fatty acids, and the neutral fatty matter. The acids are removed by treatment with either barium hydroxide or potassium carbonate, which is also employed again after decomposition of the fats by the lipase of powdered *Ricinus* or *Chelidonium* seeds, previously freed from fat.

Croton-resin is an almost colourless or pale reddish-yellow, dusty, odourless powder, softening at 80—90°, and exhibiting a bitter and, subsequently, an intense and persistent burning flavour. It dissolves sparingly in water and in almost all proportions in organic solvents with the exception of light petroleum, and is highly poisonous, besides exerting a vesicating action. With boiling concentrated hydrochloric acid its alcoholic solution gives a rose-red and then a dark red coloration, a peculiar odour of mould being emitted; with concentrated alcoholic sulphuric acid it gives a grass-green coloration in the hot. The iodine number is 76·98, and $[\alpha]_D$ in chloroform varies for different preparations from +49·96° to 63·23°. Analysis and determination of the molecular weight in naphthalene solution lead to the formula $C_{36}H_{54}O_9$. The individuality of the product obtained is not established, and little is yet known concerning its chemical character (compare Paal and Roth, A., 1909, i, 358).

T. H. P.

Synthesis of a Glucoside of Paeonol. Y. ASAHINA and G. SHIRABE (*J. Pharm. Chim.*, 1916, [vii], **13**, 222).—By means of

β-acetylbromoglucose, the authors have obtained *paeonyl-β-glucoside*, $COMe\cdot C_6H_3(OMe)\cdot O\cdot C_6H_{10}O_5,2H_2O$, in a crystalline state, prismatic needles, m. p. 118°, $[\alpha]_D$ −79°. The crystals lose their water of crystallisation at 59° and become opaque. The glucoside is readily hydrolysed by mineral acids and by emulsin, and is thus not identical with the glucoside which occurs naturally in the fresh root of *Paeonia Moutan*, which is not decomposed by emulsin (compare Péron, A., 1911, ii, 426). *Tetra-acetylpaeonyl-β-glucoside* crystallises in silky needles, m. p. 146°, $[\alpha]_D$ −44·1°.

W. G.

Biochemical Synthesis of a Galactoside of Saligenin, β-Salicylgalactoside. EM. BOURQUELOT and A. AUBRY (*Compt. rend.*, 1916, **162**, 610—612; *J. Pharm. Chim.*, 1916, [vii], **13**, 273—279).—*β-Salicylgalactoside* has been synthesised by the same method as that employed for β-salicylglucoside (compare A., 1913, i, 747), galactose being used instead of dextrose. Attempts to obtain it in a crystalline state were not successful. It has $[\alpha]_D$ −11·3° and is readily hydrolysed by emulsin or dilute sulphuric acid. With strong sulphuric acid its aqueous solution gives a red coloration, and with ferric chloride it gives a violet coloration. If a few drops of a glycerol maceration of *Russala delica* are added to its aqueous solution it slowly develops first a yellow and then a reddish-brown coloration. The last two reactions indicate that the phenolic group is still free in the galactoside. W. G.

The Isomeric Acetyl Derivatives of Nataloin and Homonataloin. E. LÉGER (*Compt. rend.*, 1916, **162**, 506—508; *J. Pharm. Chim.*, 1916, [vii], **13**, 313—317. Compare A., 1914, i, 309, 707). —A discussion of the constitution of the β-, γ-, and δ-penta-acetylnataloins and homonataloins and of their relationship to the three penta-acetylglucoses (compare Tanret, A., 1895, i, 322). The author now considers that these isomerides should be designated by the names *dl*-penta-acetylnataloin, α-penta-acetylnataloin, and β-penta-acetylnataloin respectively, similar names being adopted for the derivatives of homonataloin. W. G.

Some Derivatives of Coumarin. FRANCIS D. DODGE (*J. Amer. Chem. Soc.*, 1916, **38**, 446—457).—Just as æsculetin unites with sodium hydrogen sulphite to form sodium dihydroæsculetinsulphonate (Liebermann and Wiedermann, A., 1901, i, 736), so coumarin and limettin readily yield sulphonic compounds with interesting properties.

When coumarin is warmed with 20% sodium hydrogen sulphite it dissolves, and the solution deposits *sodium hydrocoumarinsulphonate*, $C_6H_4<\begin{matrix}O\text{——}CO\\ CH_2\cdot CH\cdot SO_3Na\end{matrix}$, on cooling, in white crystals with $1H_2O$. The analogous *potassium* salt forms white needles, and the *barium* and *copper* salts may also be obtained. The aqueous solutions of the sodium salt are neutral, but react with, and can

be titrated by, sodium hydroxide, a precipitate of coumarin being first formed, which then unites with the neutral sulphite and redissolves, thus:

$$C_6H_4<\begin{matrix}O\text{---}CO\\ CH_2\cdot \overset{|}{C}H\cdot SO_3Na\end{matrix} \xrightarrow{NaOH} C_6H_4<\begin{matrix}O\text{---}CO\\ CH:\overset{|}{C}H\end{matrix} + Na_2SO_3 + H_2O \rightarrow$$

$$C_6H_4<\begin{matrix}OH \quad SO_3Na\\ CH_2\cdot \overset{|}{C}H\cdot CO_2Na\end{matrix}.$$

A sulphonic derivative of hydrocoumaric acid is therefore formed, and through this some interesting changes are possible. On evaporation of the solution with an excess of alkali hydroxide it yields the coumarate, which indicates an expeditious process for the conversion of coumarin into coumaric acid, whereas if the dry residue left on evaporation of the solution is heated with acetic anhydride, the hydrocoumarinsulphonate is regenerated. This yields coumarin on mixing with 20% sodium carbonate or on heating at 130—160°, the following changes being therefore possible: coumarin $\rightleftarrows$ hydrocoumarinsulphonate $\rightleftarrows$ hydrocoumaric-sulphonate $\rightleftarrows$ coumaric acid.

Limettin, a dimethoxycoumarin occurring in the sediment of oil of limes, also reacts in the above way, forming *sodium hydrolimettinsulphonate*, $C_{11}H_{10}O_4,NaHSO_3,H_2O$, in large plates.

The behaviour of coumarin on hydrolysis is discussed. If an alcoholic solution is left with an excess of alkali hydroxide, hydrolysis is apparently rapid and complete. On neutralising, however, coumarin begins to form again, and this proceeds until the alkalinity increases to a certain point. If the alkali is again neutralised, more coumarin forms, and so on until an equilibrium between coumarin and the salts is reached. This formation of a lactone in an alkaline medium is not confined to coumarins, but the probability is that a substance which behaves in this way is a coumarin. J. C. W.

Synthesis of 8-Phenyl-γ-benzopyrone and a γ-Phenanthropyrone. AMY ROSE WATSON (T., 1916, **109**, 303—307).—Barger and Starling (T., 1915, **107**, 411) stated that the affinity of pyrones to iodine increases with the number of benzene nuclei in the molecule. The above pyrones have therefore been prepared by Ruhemann's chromone synthesis in order to supply further evidence on this point. 8-Phenyl-γ-benzopyrone is found to give a blue adsorption compound with iodine up to the dilution $N/4000$, and the γ-phenanthrapyrone up to $N/2000$.

2-Hydroxydiphenyl was fused with sodium (1 equiv.) and then boiled with ethyl chlorofumarate, being thus converted into *ethyl 2-diphenylyloxyfumarate*, b. p. 185°/2 mm. The free *acid*, $C_6H_4Ph\cdot O\cdot C(CO_2H):CH\cdot CO_2H$, was obtained by hydrolysis, in cream-coloured prisms, m. p. 210°, and then condensed by solution in concentrated sulphuric acid to *8-phenyl-γ-benzopyrone-2-carboxylic acid* (I), pale yellow needles, m. p. 249°, which sublimed at 250°/2 mm., and formed an *ethyl* ester, yellow needles, m. p.

133°. The elimination of carbon dioxide from the acid was effected by heating at 270°/20—30 mm., and 8-*phenyl-γ-benzopyrone* (II) was obtained in long, colourless needles, m. p. 112°, which formed a yellow *platinichloride*.

$$C_6H_3Ph{<}{\begin{array}{l}O\text{—}C\cdot CO_2H\\ \qquad\;\;\| \\ CO\cdot CH\end{array}} \longrightarrow C_6H_3Ph{<}{\begin{array}{l}O\text{—}CH\\ \qquad\;\;\| \\ CO\cdot CH\end{array}}.$$

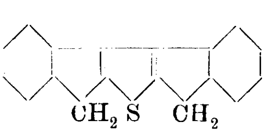
(I.) (II.)

Unlike 2-phenyl-γ-benzopyrone (flavone), the compound does not fluoresce in concentrated sulphuric acid solution.

3-Phenanthrol was converted into the sodium compound by heating with alcoholic sodium ethoxide; the dry salt was heated with ethyl chlorofumarate, and eventually converted into 3-*phenanthroxyfumaric acid*, $C_{14}H_9\cdot O\cdot C(CO_2H){:}CH\cdot CO_2H$, m. p. 223°. This gave a very small yield of a γ-*phenanthropyrone*, clusters of needles, m. p. 162—164°, on heating with phosphoric oxide in benzene. J. C. W.

Action of Sulphur on Indene, Hydrindene, and *cyclo*Pentadiene. I. Walter Friedmann (*Ber.*, 1916, **49**, 50—53).—On account of the recent publication of Scheibler (this vol., i, 65) on the chemical constituents of the bituminous tar oils containing sulphur, the author has published the following results of an incomplete investigation.

If indene is heated with sulphur a vigorous reaction ensues, two *substances* being isolable from the product, one of the composition $C_{18}H_{12}S$, possibly having the structure of a di-indenethiophen (annexed formula); this substance forms yellow leaflets, m. p. 290—292°, gives an intense green solution in sulphuric acid, yields a yellowish-red *additive* compound with tetranitromethane, and is convertible into a reddish-violet dinitro-compound, $C_{18}H_{12}S(NO_2)_2$. The other substance, $C_{36}H_{24}S$, is much less soluble than the preceding, and crystallises from cumene in pale yellow needles, m. p. 322—324°.



The action of sulphur on hydrindene in a sealed tube gave the substance $C_{18}H_{12}S$ in almost pure condition. Di*cyclo*pentadiene is converted by sulphur into a *substance* of the composition $C_{10}H_{12}S$. D. F. T.

2 : 3-Dithiosulphindene. Anna Mannessier (*Gazzetta*, 1916, **46**, i, 231—240).—The thio-*o*-benzoicsulphinide obtained by the action of phosphorus pentasulphide on *o*-benzoicsulphinide (A., 1915, i, 688) is accompanied by a small proportion of 2 : 3-dithiosulphindene, $C_6H_4{<}{\begin{array}{c}CS\\ S\end{array}}{>}S$, which may be obtained in relatively good yield by treatment of thiosaccharin with phosphorus pentasulphide,

$$C_6H_4{<}{\begin{array}{c}CO\\ SO_2\end{array}}{>}NH \longrightarrow C_6H_4{<}{\begin{array}{c}CS\\ SO_2\end{array}}{>}NH \longrightarrow C_6H_4{<}{\begin{array}{c}CS\\ S\end{array}}{>}S.$$

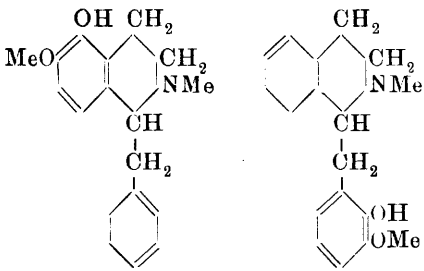
When heated with dilute alkali carbonate or hydroxide solution, 2:3-dithiosulphindene undergoes decomposition according to the scheme

$$C_6H_4{<}{}^{CS}_{S}{>}S \longrightarrow SH{\cdot}C_6H_4{\cdot}CO_2H \longrightarrow CO_2H{\cdot}C_6H_4{\cdot}S{\cdot}S{\cdot}C_6H_4{\cdot}CO_2H,$$

but only the final product, and not the intermediate thiolactic acid, could be isolated; a similar change is produced by reduction of 2:3-dithiosulphindene by means of sodium, a small proportion of *dithioindene*, $C_6H_4{<}{}^{CH_2}_{S}{>}S$ (?), m. p. 214°, being also formed.

2:3-*Dithiosulphindene*, $C_7H_4S_3$, forms intensely red, radiating needles or leaflets with golden reflection, m. p. 98°, and exhibits normal ebullioscopic behaviour in benzene. T. H. P.

Demethylation of *iso*Bebeerine. M. SCHOLTZ (*Arch. Pharm.*, 1915, **253**, 622—628. Compare A., 1915, i, 450).—When *iso*-bebeerine is heated with concentrated hydrochloric acid, the methoxyl undergoes hydrolysis with formation of a compound which contains two phenolic hydroxyl groups, and is termed *iso*-bebeeridine. The fact that the latter yields the colour reactions of catechol indicates that the two hydroxyls occupy neighbouring positions, and since *o*-cresol is obtained when bebeerine is distilled with zinc dust, the conclusion is drawn that the free hydroxyl is adjacent to a carbon side-chain which furnishes the carbon for the methyl group of the *o*-cresol. Present knowledge of the constitution of *iso*bebeerine is expressed by one or other of the annexed formulæ, in which only the third oxygen atom remains unconsidered.



iso*Bebeeridine*, $C_{17}H_{19}O_3N$, forms microscopic, yellow cubes or stellate aggregates of yellow needles, turning red at above 220°, m. p. 238—240°, but was not obtained free from the pyridine used as solvent. The following derivatives were prepared: *hydrochloride*, $C_{17}H_{19}O_3N,HCl,2H_2O$; *hydrobromide* ($+2H_2O$); *hydriodide* ($+H_2O$); *sulphate* ($+H_2O$); *perchlorate* ($+H_2O$); *methiodide*, $C_{17}H_{19}O_3N,MeI,2$—$3H_2O$, which forms yellow needles, m. p. 265—266°; and *ethiodide*, which forms yellow needles, m. p. 262—263°. The colour reactions of *iso*bebeeridine, which are described, are mostly similar to those shown by *iso*-bebeerine. T. H. P.

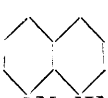
Variation with the Temperature of the Reciprocal Influence of Cinchona Alkaloids on the Rotatory Powers. C. MONTEMARTINI and F. BOVINI (*Gazzetta*, 1916, **46**, i, 153—171. Compare Oudemans, *Annalen*, 1876, **182**, 64; Hesse, *ibid.*, 147).—Appreciable differences exist between the calculated and observed rotations

of solutions containing two of the cinchona alkaloids. These differences at first diminish with rise of temperature, but subsequently appear to become constant. T. H. P.

The Rates of Conversion of the Stereoisomeric Cinchona Alkaloids into their Toxines. H. C. BIDDLE (*J. Amer. Chem. Soc.*, 1916, **38**, 901—908. Compare A., 1915, ii, 758, 759).—Measurements have been made of the rates of conversion of cinchonine and cinchonidine into cinchotoxine when heated alone or together in acetic acid solutions in sealed tubes in the absence of air at 99·4°. The results show that the specific rotatory power of cinchotoxine closely approaches, if it does not equal, the arithmetic mean of the rotatory powers of cinchonine and cinchonidine. During the conversion of these two alkaloids into the same toxine under the influence of acetic acid, the rotational values show a slight but continuous error, due to a partial racemisation of the alkaloids concerned. This effect tends to give a slightly high rate of reaction for cinchonine, whilst that for cinchonidine is slightly too low. Taking this error into account, these two rates of reaction are identical within the limits of experimental error. W. G.

A New Synthesis of Damascenine. ADOLF KAUFMANN and ERNST ROTHLEN [with B. VARGOLICI] (*Ber.*, 1916, **49**, 578—584).—The composition of damascenine, the alkaloid of *Nigella damascena*, has been definitely settled by Ewins (T., 1912, **101**, 544). In the present communication an alternative method of synthesis is described which readily permits the preparation of the alkaloid in quantity.

8-Methoxyquinoline, m. p. 46—47°, b. p. 164°/14 mm., is most conveniently prepared by the action of methyl sulphate and potassium hydroxide on commercial 8-hydroxyquinoline. When treated with methyl sulphate it readily yields the additive *product*, fine, yellow needles (annexed formula), which when oxidised with potassium permanganate in aqueous solution in the presence of magnesium sulphate passes into a mixture of *formyldamasceninic acid*, $OMe\cdot C_6H_3(NMe\cdot CHO)\cdot CO_2H$, colourless, short prisms, m. p. 194—195°, and *methoxy*-N-*methylisatin*, long, carmine-red needles, m. p. 187°. Warm dilute hydrochloric acid transforms formyldamasceninic into formic and damasceninic (2-methylamino-3-methoxybenzoic) acids, whilst the concentrated mineral acid yields *damasceninic acid hydrochloride*, colourless, flat prisms, which melt at 206—207° to a blue liquid. The alkaloid itself (methyl 2-methylamino-3-methoxybenzoate) is obtained by the action of 5% methyl alcoholic hydrogen chloride on damasceninic acid hydrochloride or on formyldamasceninic acid. It forms fine needles, m. p. 24—25°. H. W.



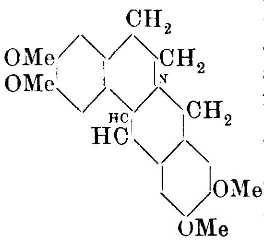
OMe $NMe\cdot O\cdot SO_3Me$

Preparation of Alkaloids of the Morphine Series and their Salts containing no *N*-Methyl Groups. F. HOFFMANN, LA ROCHE & Co. (D.R.-P., 289273; from *J. Soc. Chem. Ind.*, 1916, **35**, 438).—Morphine alkaloids containing no *N*-methyl groups are

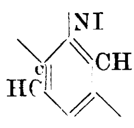
obtained by the action of a chloroformic solution of cyanogen chloride or bromide on a similar solution of the acetylated alkaloid, the temperature being maintained at 55—60° for an hour. The remainder of the process is the same as that described in the principal patent (D.R.-P., 286743). G. F. M.

Preparation of *N*-Allylnorcodeine and *N*-Allyldihydronorcodeine. F. HOFFMANN, LA ROCHE & Co. (D.R.-P., 289274; from *J. Soc. Chem. Ind.*, 1916, **35**, 438).—The *N*-allyl derivatives of norcodeine and dihydronorcodeine are obtained by introducing the allyl group into these substances. Unlike the *O*-allyl derivatives, they are therapeutically active, being energetic antidotes to morphine. G. F. M.

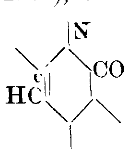
Action of Methylal on Tetrahydropapaverine. AMÉ PICTET and TSAN QUO CHOU (*Ber.*, 1916, **49**, 370—376).—Methylal condenses with tetrahydropapaverine even more readily than acetal (A., 1913, i, 1224), giving rise, however, to only one base, the lower homologue of the α- and β-coralydines, designated, consequently, norcoralydine (annexed formula). The constitution of this is determined by the production of *m*-hemipinic acid on oxidation and of a derivative of coralydine on methylation.



Norcoralydine crystallises in small, colourless leaflets, m. p. 157—158°, and forms a *hydrochloride*, soft needles, m. p. 213°, a *picrate*, slender, yellow needles, m. p. 138°, a *platinichloride*, orange-red prisms, m. p. about 231°, and a *mercurichloride*, m. p 158°. Like the similar alkaloids, canadine, corydaline, and coralydine, the base is oxidised by alcoholic iodine, yielding *dehydronorcoralydine iodide* (annexed grouping) in slender, yellow needles, m. p. 252·5°. The *nitrate*, prisms, m. p. 261°, *chloride*, m. p. 220°, and *picrate*, m. p. 255°, may be obtained from this. The free *base*, m. p. about 175°, forms a *compound* with chloroform, short, yellow needles, m. p. 215°, and a *compound* with acetone, stellar aggregates of dark yellow needles, m. p. 150°.



Just as berberine salts are converted by alkalis into dehydroberberine and oxyberberine (Gadamer, A., 1905, i, 369), so dehydronorcoralydine salts dissolve in 10% potassium hydroxide, and on warming deposit a base (m. p. about 195°, hydrochloride, m. p. 212°), and then, on acidifying the filtrate, yield *oxydehydronorcoralydine* (annexed grouping) as a precipitate. This crystallises in small, yellow prisms, m. p. 190°. Another analogy with berberine exists in the fact that dehydronorcoralydine reacts with magnesium methyl iodide to form a *base* (m. p. about 180°, *hydrochloride*, m. p. 120°), which yields dehydrocoralydine hydriodide on heating with alcoholic iodine.

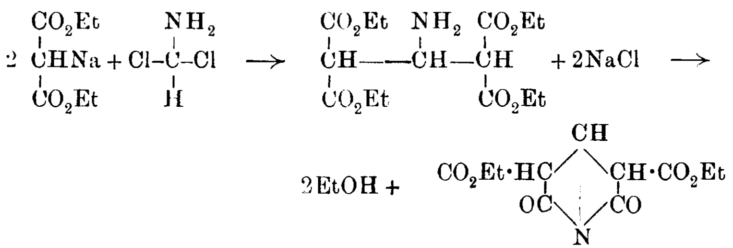


J. C. W.

The Degradation of Scopoline. Ernst Schmidt (*Ber.*, 1916, **49**, 164—168).—A claim for priority against Hess and Suchier (this vol., i, 285) in this field of work (compare Schmidt, this vol., i, 285; A., 1909, i, 173; 1906, i, 104). D. F. T.

Preparation of Diketopyrrolidine Derivatives. Chemische Fabrik auf Aktien vorm. E. Schering (D.R.-P., 289247; from *J. Soc. Chem. Ind.*, 1916, **35**, 439).—Diketopyrrolidines of the general formula $\begin{array}{l}CHR''\cdot CHR'\\ CO\text{———}CO\end{array}\!\!>NR$, where R and R' are any radicle and R'' an acid radicle, may be reduced with zinc and acetic acid, whereby two or four hydrogen atoms are taken up. As examples of the reduction products, which are valuable for the treatment of gout and rheumatism, the following are among those cited: reduction products of 4:5-diketo-3-acetyl-1:2-diphenylpyrrolidine, 4:5-diketo-3-acetyl-2-phenyl-1-*o*-methoxyphenylpyrrolidine, diketo-3-acetyl-1:2-di-*p*-methoxyphenylpyrrolidine, and ethyl 4:5-diketo-1:2-diphenylpyrrolidine-3-carboxylate. G. F. M.

A Synthesis of Pyridine Derivatives. L. Gattermann and A. Skita (*Ber.*, 1916, **49**, 494—501).—Ethyl 2:6-dioxydinicotinate is obtained in 50% yield by the condensation of the sesquihydrochloride of hydrocyanic acid with ethyl sodiomalonate, in accordance with the scheme:

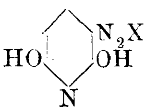


It is readily converted into dihydroxypyridine, a number of derivatives of which have been investigated.

[With L. Bühler.]—Ethyl 2:6-dioxydinicotinate forms colourless needles, m. p. 201°. The preparation presents certain difficulties, but the necessary precautions are fully described in the original text. It is best purified by means of the sparingly soluble sodium salt. On saponification with alcoholic potassium hydroxide and subsequent acidification, it yields the sparingly soluble *potassium hydrogen dinicotinate*, pale yellow leaflets. When this salt is boiled with hydrochloric acid (D 1·06) carbon dioxide is evolved, and dihydroxypyridine, long, colourless needles, m. p. 202—203° (Ruhemann gives 192—193°; Errera, ca. 195°), is formed.

3-*Nitro*-2:6-*dihydroxypyridine*, yellow needles, which decompose at 321°, is prepared by adding potassium nitrate to a solution of dihydroxypyridine in concentrated sulphuric acid. 3-*Nitroso*-2:6-

dihydroxypyridine forms pale yellow crystals, which darken at 180°, become black at 200°, and decompose at 253—254°.



Azo-dyes of the annexed formula have been prepared by coupling 2:6-dihydroxypyridine in the presence of potassium acetate with diazotised solutions of aniline (small, yellow needles), sulphanilic acid (orange-yellow needles with blue fluorescence), *p*-phenetidine (reddish-brown needles), and α-naphthylamine (red needles) respectively. H. W.

Derivatives of 2-Methylindole. M. SCHOLTZ (*Arch. Pharm.*, 1915, **253**, 629—635. Compare A., 1913, i, 520).—*Di-2-methylindylacetylacetone*,

$$NH{<}{}^{C_6H_4}_{CMe}{>}C\cdot CMe(CH_2Ac)\cdot C{<}{}^{C_6H_4}_{CMe}{>}NH,$$

prepared by the interaction of 2-methylindole and acetylacetone in acetic acid solution, forms yellow plates, m. p. 122°, and with concentrated sulphuric acid gives a yellow solution, becoming red when heated. It yields an *oxime*, $C_{23}H_{25}ON_3$, in colourless prisms, m. p. 162°, and a *semicarbazone*, $C_{24}H_{27}ON_5$, in white needles, m. p. 235°.

Benzylidenedi-2-methylindylacetylacetone,

$$C_8H_5NMe\cdot CMe(CH_2\cdot CO\cdot CH{:}CHPh)\cdot C_8H_5NMe,$$

prepared by condensing the preceding compound with benzaldehyde in presence of sodium hydroxide, forms orange-red plates, m. p. 207°, and dissolves in concentrated sulphuric acid with a yellowish-red coloration, changing to red on dilution of the liquid with water.

Furfurylidenedi-2-methylindylacetylacetone,

$$CMe(C_8H_5NMe)_2\cdot CH_2\cdot CO\cdot CH{:}CH\cdot C_4H_3O,$$

similarly prepared with the aid of furfuraldehyde, forms orange-red leaflets, m. p. 187°, and in concentrated sulphuric acid gives a brownish-red solution, which is turned bluish-violet by little, and colourless by much, water.

Cinnamylidenedi-2-methylindylacetylacetone,

$$CMe(C_8H_5NMe)_2\cdot CH_2\cdot CO\cdot CH{:}CH\cdot CH{:}CHPh,$$

similarly prepared, forms orange-red leaflets, m. p. 189°, and in concentrated sulphuric acid yields a blood-red solution, becoming colourless on dilution.

1-*Acetyldi-2-methylindyldimethylmethane*,

$$C_8H_4NMeAc\cdot CMe_2\cdot C_8H_5NMe,$$

prepared by short boiling of a solution of dimethyl-2-methylindolidenemethane (*loc. cit.*) in acetic anhydride, forms colourless plates, m. p. 224°, and dissolves in concentrated sulphuric acid, giving a yellow solution, turning orange when heated.

1-*Propionyldi-2-methylindyldimethylmethane*,

$$C_8H_4NMe(CO\cdot CH_2Me)\cdot CMe_2\cdot C_8H_5NMe,$$

similarly prepared from propionic anhydride, forms colourless, rhombic plates, m. p. 194°; 1-*butyryldi-2-methylindyldimethylmethane*, $C_{25}H_{28}ON_2$, colourless plates, m. p. 142°, and 1-*valeryldi-2-methylindyldimethylmethane*, $C_{26}H_{30}ON_2$, rhombic plates, m. p. 190°. When benzoic anhydride is used, no action takes place, but

with the anhydrides of dibasic acids, such as succinic and phthalic acids, deep violet compounds are obtained. T. H. P.

Scission of the Hydrogenated Quinoline Ring by Reduction. J. VON BRAUN and E. AUST (*Ber.*, 1916, **49**, 501—510).—According to Emde (A., 1912, i, 801), the reduction of 1 : 1-dimethyltetrahydroquinolinium chloride by sodium amalgam leads to the formation of dimethyl-*o*-propylaniline. The authors have repeated his experiments, and find the products of the reaction to be γ-dimethylaminopropylbenzene and kairoline, the constitution of the former being confirmed by its successive conversion into γ-methylaminopropylbenzene and γ-chloropropylbenzene. This course of the reaction is shown to be the more probable, since γ-phenylpropylmethylpropylamine is similarly obtained from methylpropyltetrahydroquinolinium chloride, whilst also the same amine is obtained by reducing 8- and 6-methyl-1 : 1-dimethyltetrahydroquinolinium chlorides, which is only possible if the bond between the nitrogen atom and the aromatic nucleus is ruptured during reduction.

The formation of kairoline is not caused by the alkaline nature of the liquid or by the temperature, but is due to removal of methyl by the reducing agent. This follows from the behaviour of dimethyltetrahydroquinolinium chloride towards alkali on the one hand and of methylallyltetrahydroquinolinium chloride towards sodium amalgam on the other; in the latter case, kairoline is formed in the pure state.

Contrary to the statement of Emde (*loc. cit.*), dimethyltetrahydroquinolinium iodide is attacked by sodium amalgam, although more slowly than the corresponding chloride.

Reduction of dimethyltetrahydroquinolinium chloride by sodium amalgam was performed according to Emde's directions, and the base obtained possessed the properties described by him. The crude product was treated with nitrous acid or formaldehyde, and subsequently distilled with steam, when dimethylaminopropylbenzene, b. p. 99°/14 mm., was obtained, which was further identified by means of the picrate, m. p. 99°, and methiodide, m. p. 178°. Finally, it was converted into methylaminopropylbenzene (b. p. 116°/20 mm.; m. p. of platinum salt, 188°), and the latter transformed by the action of phosphorus chloride on its benzoyl derivative into γ-*chloropropylbenzene*, b. p. 110°/20 mm.

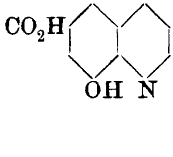
Methylpropyltetrahydroquinolinium iodide is best prepared by the interaction of methyl iodide and 1-propyltetrahydroquinoline. When converted into the corresponding chloride and reduced, it yields a mixture of bases, a portion of which is converted by formaldehyde into a non-volatile substance, which was not obtained in the pure state. On distillation with steam, γ-*phenylpropylmethylpropylamine*, $C_3H_6Ph{\cdot}NMePr$, b. p. 117—118°/14 mm., is obtained. It yields oily salts. The *methiodide* has m. p. 76°, and the corresponding *platinichloride* m. p. 173—174°.

The product of the action of silver chloride on methylallyltetrahydroquinolinium iodide is readily reduced by sodium amalgam and yelds kairoline, b. p. 118°/14 mm. (picrate, m. p. 140°; methiodide, m. p. 173·5°).

6-*Methylkairoline*, b. p. 130°/14 mm., 264—265°/756 mm., is obtained in 25% yield by the reduction of the product of the interaction of methyl iodide and 6-methylquinoline. The *picrate*, *platinichloride*, and *methiodide* melt at 152°, 175°, and 224° respectively. 8-Methylquinoline reacts less readily with methyl iodide than the corresponding 6-derivative, but the product when reduced with tin and hydrochloric acid gives a 53% yield of 8-*methylkairoline*, b. p. 127°/22 mm., 247—248°/756 mm. (*picrate*, red crystals, m. p. 156°; *platinichloride*, m. p. 208°; *methiodide*, m. p. 189°. When the quaternary iodide of either series is converted into the corresponding chloride and the latter reduced with sodium amalgam, the same amine is extracted from either crude product by treatment with water and identified by conversion into the methiodide, m. p. 150°. This amine must consequently be m-*tolylpropyldimethylamine*, $C_6H_4Me\cdot[CH_2]_3\cdot NMe_2$. H. W.

8-Hydroxyquinolinecarboxylic Acids and their Derivatives. Dihydroxyanthraquinone-3 : 7-diquinoline. St. von Niementowski and Ed. Suchard (*Ber.*, 1916, **49**, 12—24).—*m*-Amino-*p*-hydroxybenzoic acid when heated with arsenic acid, glycerol, and sulphuric acid at 140—150° for three hours is converted into 8-hydroxyquinoline-5-carboxylic acid, a microcrystalline, yellow powder, m. p. 301°, carbon dioxide being lost at a slightly higher temperature; *hydrochloride*, $C_{10}H_7O_3N,HCl,H_2O$, lustrous needles or prisms, decomp. at 260° with effervescence; *sulphate*, with $2H_2O$, a microcrystalline, yellow solid, m. p. 240°; *barium* salt, with $2H_2O$, needles; *ammonium* salt slowly yields ammonia to the air at the ordinary temperature; *ethyl* ester, prepared by the action of alcohol in the presence of much sulphuric acid, colourless needles, m. p. 125°. When heated for two hours with sulphuric acid at 150° the acid undergoes sulphonation, with concurrent loss of the carboxyl group, the product, $C_9H_5N(OH)\cdot SO_3H,2H_2O$, being probably identical with the 8-hydroxyquinoline-5-sulphonic acid described by Claus (Claus and Posselt, A., 1890, 523; Claus and Baumann, A., 1897, i, 633); this was accompanied by a *substance*, m. p. 272—278°. Oxidation in alkaline solution with potassium permanganate converted the hydroxyquinolinecarboxylic acid into quinolinic acid. The above results indicated the identity of this 8-hydroxyquinoline-5-carboxylic acid with the hydroxyquinolinecarboxylic acid obtained by Lippmann and Fleissner (A., 1887, 63, 1119) from *o*-hydroxyquinoline and carbon tetrachloride, and the identity was confirmed by a m. p. determination with a mixture of the acids prepared by the two methods.

Condensation of the isomeric *p*-amino-*m*-hydroxybenzoic acid with glycerol by heating with arsenic acid and sulphuric acid at 155—160° produced 8-*hydroxyquinoline*-6-*carboxylic acid* (formula annexed), a granular powder, m. p. 284°, which is more stable than its isomeride described above, and can, indeed, be sublimed without decomposition; *hydrochloride*, bronze-yellow, crystalline powder of metallic lustre, m. p. 312°; *sulphate*, yellow, microcrystalline powder, m. p. 307°; *phos-*

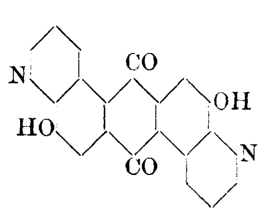


phate, $(C_{10}H_7O_3N)_3,H_3PO_4,\frac{1}{2}H_2O$, greyish-yellow, microcrystalline powder, m. p. 285°; *ammonium* salt, decomposes slowly at the ordinary temperature and instantly at 120°; *silver hydrogen* salt, $C_9H_6ON\cdot CO_2Ag,C_{10}H_7O_3N$, grey; normal *silver* salt,

$$C_9H_6ON\cdot CO_2Ag,$$

microcrystalline, greyish-yellow solid; *barium* salt, grey, crystalline solid; *ethyl* ester, needles or leaflets, m. p. 147°.

Although on account of its relative instability 8-hydroxyquinoline-5-carboxylic acid was not convertible into a dihydroxyanthraquinonediquinoline, the isomeric 8-hydroxyquinoline-6-carboxylic acid when heated with sulphuric acid and phosphoric oxide for four hours at 240° undergoes condensation to a substance of the composition $C_{20}H_{10}O_4N_2$, probably 2 : 6-*dihydroxyanthraquinonyl-3 : 7-diquinoline* (formula annexed), golden-yellow needles, m. p. 386° (decomp.); *sulphate*, metallic lustre. This compound is reduced in alkaline solution by sodium hyposulphite to a violet solution of the corresponding hydroxyanthranol derivative, which imparts a permanent yellow colour to cotton.



As a result of the above investigation, five of the six possible 8-hydroxyquinolinecarboxylic acids are now known, and in three cases the structure has been determined.

D. F. T.

Preparation of Chloro-derivatives of *N*-Dihydro-1 : 2 : 2′ : 1′-anthraquinoneazine and its Substitution Products. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 289279; from *J. Soc. Chem. Ind.*, 1916, **35**, 415).—The chlorides of sulphur act on *N*-dihydro-1 : 2 : 2′ : 1′-anthraquinoneazine and its substitution products, either in presence of a catalyst or otherwise, solely as chlorinating agents provided that sufficiently high temperatures are employed. Hitherto only sulphur-containing products have been obtained from anthraquinone derivatives by this method (see D.R.-P., 224500, 240792, 245768, 246867, and 271947).

G. F. M.

Formation of *iso*Oxazolones from Aldehydes and Oximinolævulic Acid. OTTO DIELS and KARL SCHLEICH (*Ber.*, 1916, **49**, 284—285).—With the hope of obtaining large quantities of benzylidenediacetyl, the authors condensed oximinolævulic acid with benzaldehyde, expecting to get a compound,

$$CHPh:CH\cdot CO\cdot C(:N\cdot OH)\cdot CH_2\cdot CO_2H,$$

which would yield the desired substance on hydrolysis. The product of the condensation was found to be, however, a benzylidene-*iso*oxazolone.

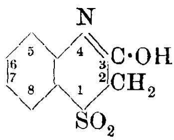
The necessary oximinolævulic acid was obtained by shaking ethyl acetylsuccinate with dilute potassium hydroxide, adding sodium nitrite to the solution, and then acidifying with sulphuric acid. Condensation with benzaldehyde was effected in concentrated hydrochloric acid solution, and 5-*keto-3-acetyl-4-benzylidene-*

4 : 5-*dihydro*isoo*xazole*, $O\!<\!\begin{matrix}N{=}CAc\\ CO\cdot C{:}CHPh\end{matrix}$, was obtained in sulphur-yellow, prismatic leaflets, m. p. 124°, which formed a *semicarbazone*, $C_{13}H_{12}O_3N_4$, bundles of yellow needles, m. p. 212° (decomp.), and a *compound*, $C_{14}H_{13}O_4N_3$, small, yellow needles, m. p. 200° (decomp.) with methyl hydrazinecarboxylate.

Condensation with furfuraldehyde yielded 5-*keto*-3-*acetyl*-4-*furfurylidene*-4 : 5-*dihydro*isoo*xazole*, $C_{10}H_7O_4N$, which crystallised in curved, deep yellow needles, m. p. 126°, with a peculiar odour, and formed a *semicarbazone*, in pale brown leaflets, m. p. above 300°. Anisaldehyde gave rise to 5-*keto*-3-*acetyl*-4-*anisylidene*-4 : 5-*dihydro*isoo*xazole*, $C_{13}H_{11}O_4N$, which formed long, yellow, curved needles, m. p. 162°. J. C. W.

Action of Aldehydes on Primary Hydroxy-amines. MORITZ KOHN (*Ber.*, 1916, **49**, 250—251).—The author had already studied the action of formaldehyde and benzaldehyde on diacetonalkamine (A., 1904, i, 932, 933), and assigned to the products the constitution of 2 : 4 : 5 : 6-tetrahydro-1 : 3-oxazines, whereas Hess and Uibrig (this vol., i., 124) made no mention of this work and called the products alkylidenediacetonalkamines. J. C. W.

Heterocyclic Sulphones. II. Some Derivatives of Sulphazone. M. CLAASZ (*Ber.*, 1916, **49**, 350—363. Compare A., 1912, i, 389). —A number of reactions and derivatives of "sulphazone" have been studied, and it now appears that the compound is a 3-hydroxybenzsulphonazine of the annexed constitution.



When sulphazone is added to 60% nitric acid at 70°, it dissolves and, on cooling, deposits the *nitrate* in very pale yellow, glistening leaflets, decomp. 172°.

The methylene group is very reactive towards halogens. Thus, chlorine and bromine in acetic acid yield 2 : 2-*dichlorosulphazone*, iridescent leaflets, m. p. 182°, and 2 : 2-*dibromosulphazone*, hard prisms, m. p. 214°. From the latter, alcoholic sodium iodide produces the 2 : 2-*di-iodo*-compound, soft, yellow needles, m. p. 217°. An alkaline solution of iodine in potassium iodide converts sulphazone into 2-*iodosulphazone*, a microcrystalline powder, m. p. 196°. These compounds dissolve in alkali hydroxides, but are precipitated unchanged on acidifying. They do not react with nitrous acid or diazonium salts, but silver nitrate precipitates the halogen completely.

The effect of nitrating and sulphonating agents, however, is to give derivatives in which the benzene ring is entered in position 7. 7-*Nitrosulphazone* forms well-developed, colourless leaflets, m. p. 219—220° (decomp.), and *sulphazone*-7-*sulphonic acid* crystallises in prisms. That position 2 is open in these derivatives is shown by the fact that they couple with diazonium salts, and that 2 : 2-*dibromo*-7-*nitrosulphazone*, white needles, m. p. 261°, can be obtained either by brominating the nitro-compound or nitrating the above

dibromide. Similarly, just as sulphazone itself yields a 2-*oxime* when treated with nitrous acid, slender, yellow needles, m. p. 203° (decomp.), so 7-*nitrosulphazone-2-oxime*, pale yellow nodules, m. p. 198° (decomp.), can be obtained either from this by nitration or from the above nitro-compound. The oximes give blue lakes with iron.

Sulphazone can also be methylated by means of methyl iodide and sodium hydroxide. The 3-*methyl ether* forms colourless needles, m. p. 210°.

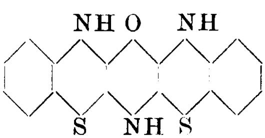
The above nitrosulphazone is readily reduced by tin and hydrochloric acid to 7-*aminosulphazone*. This is an amphoteric substance, and forms soft needles, m. p. 226°; the *hydrochloride* forms white leaflets, m. p. 258° (decomp.), and the *acetyl* compound colourless prisms, m. p. 267°. The base couples slowly with diazonium salts in neutral or acetic acid solution in position 6, but quickly in alkaline solutions in position 2. Moreover, it may be diazotised itself and then coupled, and consequently it can yield many dyes. The bisazo-dyes are particularly good substantive dyes for cotton. For example, 7-*amino*-6-p-*nitrobenzeneazo*-2-p-*sulphobenzeneazosulphazone*,

$$NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_2(NH_2)<\begin{matrix} NH\cdot C\cdot OH \\ \quad\;\, \| \\ SO_2-C\cdot N_2\cdot C_6H_4\cdot SO_3H \end{matrix},$$

is a dark brown dye which is obtained by first applying diazotised *p*-nitroaniline in acetic acid solution, and then diazotised sulphanilic acid in alkaline solution, whilst *sulphazone-7-azo-β-naphthol*, $OH\cdot C_{10}H_6\cdot N_2\cdot C_6H_3<\begin{matrix} N{=}C\cdot OH \\ \quad\;\, | \\ SO_2\cdot CH_2 \end{matrix}$, is a Bordeaux-red dye.

Attempts were made to oxidise sulphazone to the corresponding ketone, both directly and through the oxime. The result was always the opening of the heterocyclic ring and the formation of o-*sulphinoxanilic acid*, $SO_2H\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2H$, m. p. 215° (decomp.).

The oxime also gave unexpected results on reduction. It appears that the 2-amine is very reactive, and hence leads immediately to other products. Thus, reduction by means of tin and hydrochloric acid yields *dibenzthiazoxazine* in pale yellow needles, m. p. 275—278° (annexed formula), whilst ammonium sulphide gives a *compound*, $C_{16}H_{18}O_8N_4S_5$, which is a strongly electric powder, m. p. 126° (decomp.). Similarly, attempts to reduce an azo-compound to the amine also failed. Thus, 2-benzeneazosulphazone can only be reduced as far as



the *hydrazone*, $C_6H_4<\begin{matrix} N{=}C\cdot OH \\ \quad\;\, | \\ SO_2\cdot CH\cdot NH\cdot NHPh \end{matrix}$, which crystallises in pale yellow, glistening leaflets, m. p. 260° (decomp.). J. C. W.

Heterocyclic Sulphones. III. Sulphurylindoxyl. M. CLAASZ (*Ber.*, 1916, **49**, 614—621).—Sulphazone, $C_6H_4<\begin{matrix} NH\cdot CO \\ \quad | \\ SO_2-CH_2 \end{matrix}$ (A., 1912, i, 390), is transformed by the action of ammonia under pressure into formic acid and *benzsulphonazoline*, $C_6H_4<\begin{matrix} NH \\ SO_2 \end{matrix}>CH_2$,

the dihydro-derivative of benzsulphonazole (Zincke and Siebert, A., 1915, i, 882). On account of the close analogy existing between the substance and the indole compounds, the author proposes the name "*sulphurylindoxyl*." A comparison of the properties of the substance with the analogously constituted indoxyl, β-cumaranone, and oxythionaphthen compounds shows a gradual decrease in activity until in benzsulphonazoline the hydrogen atoms of the methylene group are scarcely affected by the proximity of the SO_2-group; an analogous behaviour has been observed previously with open-chain compounds.

Benzsulphonazoline, obtained by heating sulphazone with 25% ammonia at 160° for four hours, forms fine needles from water or compact crystal aggregates from dilute acetic acid. It has m. p. 85—86°, b. p. 336°/768 mm. When dissolved in acetic acid and treated with the requisite quantity of bromine, it is converted into *bromobenzsulphonazoline*, $C_6H_4<\substack{NH\\SO_2}>CHBr$, pearly leaflets, m. p. 138°; with larger quantities of bromine, the *dibromo*-derivative, $C_6H_4<\substack{NH\\SO_2}>CBr_2$, glassy prisms, m. p. 130°, is obtained. These compounds are so stable that the bromine atoms cannot be removed without rupture of the molecule; silver nitrate solution, aniline, and metallic sodium in benzene solution have no action even when heated.

aci-*Nitrobenzsulphonazoline*, $C_6H_4<\substack{NH\\SO_2}>C:NO_2H$, microscopic, brown needles, m. p. 110—112°, is obtained by the nitration of benzsulphonazoline in concentrated sulphuric acid solution.

The action of nitrous oxide on a solution of benzsulphonazoline in acetic acid leads to the formation of a substance,

$$C_6H_4<\substack{NH\\SO_2}>C\left(N:C<\substack{NH\\SO_2}>C_6H_4\right)_2,$$

termed by the author "*trisulphurylisatodinitrile*," fine, pale yellow needles, which crystallise with 1 mol. of acetone, m. p. 210—211° (decomp.).

N-*Acetylbenzsulphonazoline* forms colourless prisms, m. p. 136°.

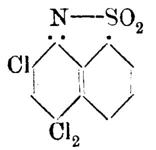
H. W.

Naphthasultam. I. *iso*Naphthasultam and Chloro-derivatives of Naphthasultam and of Dihydro- and Tetrahydronaphthasultams. TH. ZINCKE and C. JÜLICHER (*Annalen*, 1916, **411**, 195—216).—The authors show that Dannerth's so-called 1 : 8-*iso*naphthasultam, obtained by heating naphthasultam with acetic anhydride (A., 1907, i, 909), is in reality *N*-acetylnaphthasultam; consequently, his nitro-derivatives of *iso*naphthasultam are simply nitro-*N*-acetylnaphthasultams.

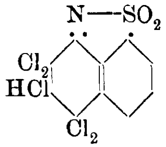
The behaviour of 1 : 8-naphthasultam towards chlorine presents extensive analogies to that of α-naphthol, a di-, tri-, or pentachloro-derivative being obtained, according to the duration and method of chlorination.

2 : 4-*Dichloro*-1 : 8-*naphthasultam*, $C_{10}H_5O_2NCl_2S$, glistening leaflets, m. p. 195°, is obtained by treating naphthasultam

suspended in glacial acetic acid with the calculated quantity of chlorine; by using a smaller amount, the chloro-derivative and unchanged naphthasultam are obtained. It dissolves in aqueous sodium hydroxide with a yellow colour, as does naphthasultam itself, and forms an *acetyl* derivative, colourless leaflets, m. p. 170°. By further chlorination in chloroform solution it is converted into a trichloro-derivative, which can also be prepared from the naphthasultam itself in the same solvent without cooling. The trichloro-derivative liberates iodine from potassium iodide in acetic acid solution, and is doubtless 2:4:4-*trichloro*-1:4-*dihydro*-1:8-*naphthasultam* (annexed formula). It exists in two forms, a yellow, labile form and a colourless, stable form, both of which, especially the latter, are phototropic. The coloured modification crystallises from chloroform in stout, yellow needles or prisms, and from benzene in plates containing benzene of crystallisation. It melts in a bath heated at 195°, but immediately re-solidifies, and then has m. p. about 250° (decomp.), having undergone conversion into the stable form. This change is also effected in boiling glacial acetic acid solution, this being the best method of securing the colourless form, leaflets or flat needles, m. p. about 252° (decomp.).



Both modifications of the trichlorodihydronaphthasultam (the colourless form very slowly) are converted by further chlorination in glacial acetic acid into 2:2:3:4:4-*pentachloro*-1:2:3:4-*tetrahydro*-1:8-*naphthasultam* (annexed formula), which can also be obtained by the exhaustive chlorination of the naphthasultam in the same solvent without cooling. It crystallises in plates, m. p. 211°, or from benzene in colourless needles and prisms containing benzene of crystallisation. When heated with pyridine or with sodium acetate and glacial acetic acid, it loses hydrogen chloride and is converted into 2:3:4:4-*tetrachloro*-1:4-*dihydro*-1:8-*naphthasultam*, $C_{10}H_3O_2NCl_4S$, colourless needles, m. p. 254°. In glacial acetic acid the tetrachloro-derivative is reduced by stannous chloride and the pentachloro-derivative by concentrated aqueous sodium hydrogen sulphite, the product in each case being 2:3:4-*trichloro*-1:8-*naphthasultam*, $C_{10}H_4O_2NCl_3S$, colourless needles, m. p. 235°, which does not yield an acetyl derivative, but forms a *sodium* salt, yellow leaflets.

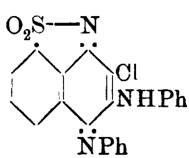


The pentachlorotetrahydronaphthasultam is reduced to 2:4-dichloro-1:8-naphthasultam by stannous chloride.

By shaking a suspension of white or yellow trichlorodihydronaphthasultam in alcohol with two parts of aniline, 2-*chloro*-3-*anilinonaphthasultamquinoneanil* (annexed formula), orange-red leaflets or broad needles, m. p. 215° (decomp.), is formed, which is converted by heating with alcohol and hydrochloric or sulphuric acid into 2-*chloro*-3-*anilinonaphthasultamquinone*,

$C_{16}H_9O_3N_2ClS$,

dark violet leaflets, m. p. 265° (decomp.), insoluble in alkalis. By warming with alcohol and aniline, tetrachlorodihydro- and pentachloro-



tetrahydro-naphthasultams yield, the latter with preliminary loss of hydrogen chloride, 2 : 4 : *4-trichloro-3-anilino-1 : 4-dihydro-1 : 8-naphthasultam*, $C_{16}H_9O_2N_2Cl_3S$, brown needles, blackening at 200°, which is converted into the preceding dianilide by warming with more aniline. C. S.

Tetrabromo-*o*-phenylenediacetamide. C. Loring Jackson and Sydney Adams Beggs (*J. Amer. Chem. Soc.*, 1916, **38**, 685—687).—It was hoped to prepare tetrabromo-*o*-phenylenediamine by brominating acetylated dibromo-*o*-phenylenediamine, and then hydrolysing the amide. Instead of removing the acetyl groups, however, hydrolytic agents removed the elements of water and a benziminazole derivative was formed.

Acetylation of 4 : 6-dibromo-*o*-phenylenediamine in the cold yielded *4 : 6-dibromo-2-aminoacetanilide*, $NH_2\cdot C_6H_2Br_2\cdot NHAc$, in white needles, m. p. 189°. The diamide, which is formed at higher temperatures (A., 1906, i, 307), was converted into *tetrabromo-*o*-phenylenediacetamide*, $C_6Br_4(NHAc)_2$, by boiling with bromine and acetic acid. The compound forms white prisms, not molten at 280°, and yields *tetrabromo-3-acetyl-2-methylbenziminazole*,

$$C_6Br_4{<}{\scriptstyle NAc \atop N}{>}CMe,$$

white crystals, m. p. 265—266°, when heated with dilute sulphuric acid or alcoholic ammonia. J. C. W.

Constitution of Anthranil. X. Gustav Heller (*Ber.*, 1916, **49**, 523—548. Compare A., 1915, i, 844).—It has been shown that the simple acylanthranils, and also oxalyl- and malonyl-bisanthranils, are derivatives of the lactam form of anthranil. Attempts to prepare similar derivatives are now described. The constitution of anthranil is very fully discussed, and it is shown that the majority of the reactions of the substance are most readily explained by the adoption of the lactam formula for the base.

[With Hermann Heine.]—*Ethyl carbonylbisanthranilate*,

$$CO(NH\cdot C_6H_4\cdot CO_2Et)_2,$$

colourless needles, m. p. 135°, is obtained by the action of carbonyl chloride on ethyl anthranilate, and when hydrolysed with aqueous alcoholic potassium hydroxide, and subsequently acidified, yields *2 : 4-diketotetrahydroquinazoline-3-*o*-benzoic acid*,

$$C_8N_2H_4O_2\cdot C_6H_4\cdot CO_2H,$$

colourless rods, m. p. 292—293°, with evolution of carbon dioxide.

Acetanthranil is obtained by the action of acetic anhydride on methylenedianthranilic acid. Acetanthranilic acid is converted by heating with glacial acetic acid and anhydrous sodium acetate into a compound of acetanthranilic acid and sodium acetanthranilate (compare Heller and Fiesselmann, A., 1902, i, 779).

Bisanthranil, ${\scriptstyle CO \atop C_6H_4}{>}N\cdot N{<}{\scriptstyle CO \atop C_6H_4}$, is obtained by the action of acetic anhydride on *o*-hydrazobenzoic acid. The product is generally more or less contaminated with indazolylbenzolactone, the purest product being obtained (at the expense of the yield) when

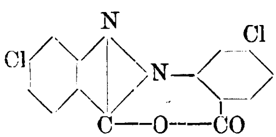
the duration of heating is short. The pure substance forms needles, which melt at 180—181°, gradually solidify when heating is continued, and finally melt at 295° (m. p. of the indazolyl lactone). The same change appears to occur very slowly at the ordinary temperature. When oxidised with chromic acid in glacial acetic acid at 60—70°, it gives a quantitative yield of *o*-azobenzoic acid.

Anthraniloacetanthranilic acid, $\begin{matrix}\mathrm{CO}-\\ |\\ \mathrm{C_6H_4}\end{matrix}\!\!>\mathrm{N\cdot NAc\cdot C_6H_4\cdot CO_2H}$, is obtained from the mother liquors of the above preparation, and has m. p. 197° (decomp.), passing at the same time into indazolylbenzolactone. When heated for a short time with acetic anhydride it is converted into bisanthranyl. A reverse transformation into *o*-hydrazobenzoic acid only occurs to a small extent. Hydrolytic agents convert it into indazolylbenzoic acid and its lactone.

A mixture of bisanthranyl and indazolylbenzoic lactone is obtained by warming *o*-azoxybenzaldehyde with glacial acetic acid.

4-*Chloro*-2-*nitrobenzamide* forms long, colourless needles, m. p. 172°.

4 : 4′-*Dichloro*-2 : 2′-*hydrazobenzoic acid*, microscopic needles, m. p. 267° (decomp.), after darkening at 250°, is obtained by the reduction of an alkaline solution of 4-chloro-2-nitrobenzoic acid by zinc dust. When heated with acetic anhydride on the water-bath, it is converted into 4 : 4′-*dichloro*-2-*indazolylbenzolactone* (annexed formula), fine needles, m. p. 335°. The latter is only slowly dissolved by dilute sodium hydroxide, and the solution on acidification yields *dichloroindazolylbenzoic acid*, needles, which show the m. p., 335°, of the lactone.



When benzenesulphonyl chloride is slowly added to a well-cooled solution of anthranilic acid in pyridine, a mixture of *o*-phenylsulphaminobenzoylanthranil,

$$\begin{matrix}\mathrm{CO}-\\ |\\ \mathrm{C_6H_4}\end{matrix}\!\!>\mathrm{N\cdot CO\cdot C_6H_4\cdot NH\cdot SO_2Ph},$$

and diphenylsulphodianthranilide, $\begin{array}{l}\mathrm{PhSO_2\cdot N-C_6H_4-CO}\\ \qquad\quad\;\; |\qquad\qquad\;\; |\\ \qquad\quad\mathrm{CO-C_6H_4-N\cdot SO_2Ph}\end{array}$

m. p. 263°, is obtained. H. W.

Simple Method for the Preparation of Substituted Indigotins. Fr. Bodinus (*Chem. Zeit.*, 1916, **40**, 326).—Indigotin and substituted indigotins are readily obtained by the reduction of ω-chloro-*o*-nitroacetophenone or of substituted chloronitroacetophenones by boiling with zinc and 30% acetic acid. Thus, from ω-4-*dichloro*-5-*acetylamino*-2-*methylacetophenone*, prepared by chlorinating *p*-acetotoluidide in glacial acetic acid solution and condensing the *m*-chloro-*p*-acetotoluidide, m. p. 116° produced with chloroacetylchloride, the 6-*nitro-derivative* was obtained as yellow, silky

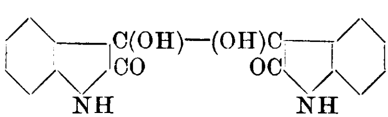
needles, m. p. 198—199°, and this substance on reduction with zinc in acetic acid solution gave a blue precipitate of 6 : 6′-*dichloro*-7 : 7′-*diacetylamino*-4 : 4′-*dimethylindigotin*. The indigotin is formed through the intermediate production of an indoxyl, as indicated in the following scheme:

$$C_6H_4<{}^{NO_2}_{CO\cdot CH_2Cl} \xrightarrow{H} C_6H_4<{}^{NH_2}_{CO\cdot CH_2Cl} \longrightarrow HCl + C_6H_4<{}^{NH}_{CO}>CH_2,$$

and the latter then undergoes oxidation in the usual way. The preparation of 7 : 7′-*diphthalylamino*-4 : 4′ : 6 : 6′-*tetramethylindigotin* is also described, starting from 4-*phthalylamino*-m-*xylene*, m. p. 159·5°, which on condensation with chloroacetyl chloride yields the corresponding chloro-ketone, m. p. 193°. This on nitration gives yellow needles of ω-*chloro*-6-*nitro*-5-*phthalamino*-2 : 4-*dimethylacetophenone*, m. p. 200°, which on reduction is converted into the above-mentioned indigotin, having a bright, bluish-green colour. By similar methods any other desired indigotin substitution product may be prepared. G. F. M.

The Probable Identity of Laurent's Indine with the *iso*-Indigotin of Wahl and Bagard. Léon Lefèvre (*Bull. Soc. chim.*, 1916, [iv], **19**, 111—113).—The author considers that the indine prepared by Laurent by the action of heat on isatyde or by the action of potassium hydroxide on isatyde sulphide (compare *Ann. Chim. Phys.*, 1841, [iii], **3**, 471) is identical in constitution with the *iso*indigotin prepared by Wahl and Bagard by the condensation of oxindole and isatin (compare A., 1909, i, 330). This is confirmed by a comparison of their properties and by the fact that indine was obtained by Knop by the dehydration of hydrindic acid (dioxindole) (compare *Bull. Soc. chim.*, 1866, [ii], **6**, 650). W. G.

The Constitution of Isatyde and Isatan. Léon Lefèvre (*Bull. Soc. chim.*, 1916, [iv], **19**, 113—116).—The author considers that the constitution assigned to isatyde by Heller (compare A., 1904, i, 416), based on the analogy between its synthesis by the condensation of isatin and dioxindole, and the synthesis of quinhydrone by the condensation of quinone and quinol, is not in accord with the lack of analogy between the properties of isatyde and quinhydrone, or with the transformation of isatyde into indine and isatin by heat. He assigns to isatyde the constitution I,



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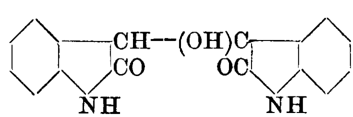


(II.)

which permits of a ready explanation of the reactions of this substance. By analogy, isatan has the constitution II. W. G.

meri-**Quinonoid Salts.** A. HANTZSCH (*Ber.*, 1916, **49**, 511—523. Compare A., 1913, i, 393, 903; 1914, i, 91).—In part a reply to Kehrmann (A., 1913, i, 298, 522, 1241; 1914, i, 331). The previous assumption that the green and brownish-red methylphenazonium iodides are chromoisomeric was based on Kehrmann's analyses, and loses its significance now that analytical errors have been discovered. The most convincing evidence of the *meri*-quinonoid nature of the green methylphenazonium salts is derived from the observation that they are formed by the addition of 1 mol. of halogen to methyldihydrophenazine and quantitatively oxidised to the ordinary methylphenazonium salts by a second molecule.

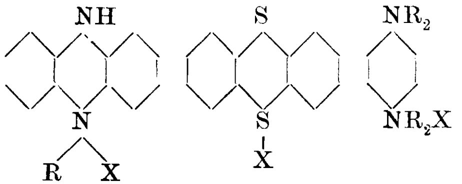
N-*Methyldihydrophenazine*, $C_6H_4<\genfrac{}{}{0pt}{}{NH}{NMe}>C_6H_4$, is prepared by the energetic reduction of methylphenazonium salts by zinc dust and dilute hydrochloric acid in an oxygen-free atmosphere. In the absence of oxygen it melts sharply at 164°, but when heated in the usual manner darkens at about 130° and melts at a slightly higher temperature. It yields colourless salts which become green on exposure to air, and is converted by bromine or iodine (1 mol. to 2 mols. of the base) into the green salts. The quantitative conversion of the *meri*-quinonoid into *holo*-quinonoid salts is readily followed by the action of iodine on a solution of the green, *meri*-quinonoid *bromide*, $C_{26}H_{24}N_4Br_2$, but the change only occurs smoothly in the presence of water. In the absence of the latter, the greenish-black, *meri*-quinonoid tri-iodide, $C_{13}H_{11}N_2I_3 + C_{13}H_{13}N_2I + C_2H_5 \cdot OH$, is precipitated from alcoholic solution.

The formation of *meri*-quinonoid from *holo*-quinonoid salts in the absence of reducing agents has been observed in a number of cases. Thus, *methylphenazonium chloride*, pale orange crystals, is transformed by hydrogen chloride in alcoholic solution into the *hydrochloride* of the *meri*-quinonoid salt, $C_{26}H_{24}N_4Cl_2,2HCl$, which readily loses hydrogen chloride to yield the neutral *meri*-quinonoid chloride, $C_{26}H_{24}N_4Cl_2$, both salts being coloured green. A similar transformation is observed when the *holo*-quinonoid chloride, bromide, or methosulphate, but not the iodide or perchlorate, is heated above 100°, or when a solution of the yellow chloride in chloroform is warmed. The green salts are always contaminated with decomposition products, from which the hydrogen necessary for reduction is derived.

Attempts to isolate the free *meri*-quinonoid base are also described; the results show, however, that the base of the simple *meri*-quinonoid phenazonium salts resolves itself spontaneously into phenazine and hydrophenazine, whilst that of the *meri*-quinonoid methylphenazonium salts decomposes into methylphenazonium salt and methyldihydrophenazine.

By a comparison of the optical behaviour of solutions of *meri*-quinonoid salts with those of quinhydrones, the author is led to

doubt the conception of the intensely coloured derivatives of phenazines, thiazines, *p*-diamines, and thianthrenes as molecular additive products resembling quinhydrones, and tentatively suggests that these salts may be simple, unimolecular compounds with an unsaturated nitrogen or sulphur atom, to the unsaturated state of which the intense colour is attributed. The annexed formulæ are proposed. Owing to experimental difficulties, attempts to obtain evidence of molecular complexity by determinations of molecular weight or electrical conductivity have so far been unsuccessful. H. W.



So-called phenazonium salt. *meri*-Quinonoid thianthronium salt. Wurster's salt

Action of Certain Acid Reagents on the Substituted Carbamides and Thiazole. II. F. B. DAINS, R. C. ROBERTS, and R. Q. BREWSTER (*J. Amer. Chem. Soc.*, 1916, **38**, 131—140. Compare A., 1900, i, 390).—The effect of acyl reagents on the groupings $\cdot NH\cdot CO$(or S)$\cdot NH$ and $\cdot NH\cdot C(SR)\colon NR$, in both open-chain and ring compounds, has received further attention.

Disubstituted carbamides were found to yield amidine hydrochlorides when heated with acyl chlorides. Thus, at 170°, di-*o*-tolylcarbamide and benzoyl chloride give benz-*o*-toluidide and *α-di-*o*-tolylbenzenylamidine*, $C_7H_7\cdot N\colon CPh\cdot NH\cdot C_7H_7$, which forms slender, white needles, m. p. 87—88°. Diphenylcarbamide and *iso*valeryl chloride react at 140° to form *α-diphenyl*iso*pentenylamidine*, $CHMe_2\cdot CH_2\cdot C(NHPh)\colon NPh$, m. p. 103° (*platinichloride*, m. p. 207°; *picrate*, m. p. 144—145°). Di-*m*-tolylcarbamide and *iso*valeryl chloride react at 140—150° to form *α-di-*m*-tolyl*iso*pentenylamidine*, slender needles, m. p. 102° (*platinichloride*, m. p. 214°), whilst di-*p*-tolylcarbamide yields *α-di-*p*-tolyl*iso*pentenylamidine*, m. p. 91—92° (*hydrochloride*, m. p. 175°; *platinichloride*, m. p. 199°). Di-*p*-tolylcarbamide and *m*-nitrobenzoyl chloride yield *α-di-*p*-tolyl-*m*-nitrobenzenylamidine*,

$$NO_2\cdot C_6H_4\cdot C(NH\cdot C_7H_7)\colon N\cdot C_7H_7,$$

slender, yellow needles, m. p. 137°.

Further examples of the action of hot acyl chlorides on thiocarbamides are given. Thus, di-α-naphthylthiocarbamide yields with acetyl chloride at 90° α-naphthylthiocarbimide and acet-α-naphthalide, and with benzoyl chloride at 160° the thiocarbimide and benz-α-naphthalide. Thiocarbamide and phthalyl chloride react at 160° to form phenylcarbimide and phthalanil, but diacyl chlorides do not react like the simple chlorides with oxygen carbamides. For example, diphenylcarbamide and phthalyl chloride yield phthalanil and a little phenylcarbamide and carbonyl chloride, but no amidine.

The action of diphenylcarbamyl chloride on various carbamides

and thiocarbamides is described. The results amplify those obtained by Dixon (T., 1899, **75**, 405). Dixon and Taylor (T., 1912, **101**, 2522) also showed that trisubstituted thiocarbamides can be readily acylated, and this is confirmed by the formation of the *compound*, $CO(NPh\cdot CS\cdot NPhEt)_2$, by the action of a benzene solution of carbonyl chloride on diphenylethylcarbamide in the presence of pyridine. The compound crystallises in slender needles, m. p. 166°, and the sulphur in it cannot readily be removed. Trisubstituted thiocarbamides will only react with carbamyl chlorides at high temperatures, however, giving thiocarbimides and tetrasubstituted oxygen carbamides. Thus, diphenylmethylthiocarbamide yields with diphenylcarbamyl chloride at 150° phenylthiocarbimide and *triphenylmethylcarbamide*, $NPh_2\cdot CO\cdot NPhMe$, m. p. 105°, and with phenylmethylcarbamyl chloride, diphenyldimethylcarbamide; diphenylethylthiocarbamide gives with diphenylcarbamyl chloride triphenylethylcarbamide, and with phenylmethylcarbamyl chloride *αβ-diphenyl-α-methyl-β-ethylcarbamide*, NPhMe·CO·NPhEt, m. p. 74°, which was also synthesised by treating phenylethylamine with phenylmethylcarbamyl chloride in the presence of pyridine at 140°.

As further examples of the acylation of *iso*thiocarbamide ethers, the formation of *acetylmethyl*iso*diphenylthiocarbamide*,

SMe·C(NPhAc):NPh,

cubes, m. p. 71°, by the action of acetic anhydride or acetyl chloride on methyl*iso*diphenylthiocarbamide, and the production of m-*nitrobenzoylethyl*iso*di*-o-*tolylthiocarbamide*,

$$SEt\cdot C(:NC_7H_7)\cdot N(C_7H_7)\cdot CO\cdot C_6H_4\cdot NO_2,$$

m. p. 122°, and of m-*nitrobenzoylmethyl*iso*diphenylthiocarbamide*, m. p. 101°, are described. These ethers do not react in the same way with carbamyl chlorides, however, but at high temperatures yield thiocarbamides, alkyl chlorides, and trisubstituted oxygen carbamides. Thus, methyl*iso*diphenylthiocarbamide and diphenylcarbamyl chloride form methyl chloride, phenylthiocarbimide, and diphenylmethylcarbamide, whilst ethyl*iso*-*o*-tolylthiocarbamide and phenylmethylcarbamyl chloride yield ethyl chloride, *o*-tolylthiocarbimide, and *phenyl*-o-*tolylmethylcarbamide*,

$$C_7H_7\cdot NH\cdot CO\cdot NMePh,$$

slender, white needles, m. p. 117°, and ethyl*iso*di-*o*-tolylthiocarbamide and diphenylcarbamyl chloride give rise to *diphenyl*-o-*tolylcarbamide*, $NPh_2\cdot CO\cdot NH\cdot C_7H_7$, m. p. 85°.

It has already been shown (*loc. cit.*; Dixon, T., 1908, **93**, 24) that allylthiocarbamides are converted into thiazoles when warmed with acyl chlorides. Some of them can be acylated if the chloride is applied in the presence of benzene and pyridine. Thus, phenylallylthiocarbamide and benzoyl chloride yield *β-benzoyl-β-phenyl-α-allylcarbamide*, $C_3H_5\cdot NH\cdot CS\cdot NBzPh$, m. p. 125°; *p*-bromophenylallylthiocarbamide and acetyl chloride form the *compound*, $C_3H_5\cdot NH\cdot CS\cdot NAc\cdot C_6H_4Br$, m. p. 86°; and *p*-chlorophenylallylthiocarbamide and acetyl chloride give *β-acetyl-β*-p-*chlorophenyl-α-allylthiocarbamide*, m. p. 84°. As examples of the thiazole synthesis, the following are described: 2-p-*bromoanilino*-5-*methyl*-

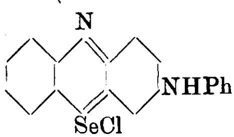
4 : 5-*dihydrothiazole*, $C_6H_4Br\cdot NH\cdot C\Big\langle\begin{matrix} N\cdot CH_2 \\ | \\ S-CHMe \end{matrix}$, by heating *p*-bromophenylallylthiocarbamide with acetyl chloride, m. p. 107°, *picrate*, m. p. 156°; 2-p-*chloroanilino*-5-*methyl*-4 : 5-*dihydrothiazole*, m. p. 116°, *hydrochloride*, m. p. 226°; 2-m-*tolylamino*-5-*methyl*-4 : 5-*dihydrothiazole*, from *m*-tolylallylthiocarbamide, m. p. 90°, *picrate*, m. p. 158°. These thiazoles are structurally related to the *iso*carbamide ethers, and therefore can be acylated. Thus, 2-anilino-5-methyl-4 : 5-dihydrothiazole reacts with benzoyl chloride in the presence of pyridine to give the *compound*,

$$NPhBz\cdot C\Big\langle\begin{matrix} N-CH_2 \\ | \\ S-CHMe \end{matrix},$$

m. p. 118°. J. C. W.

Selenazine Colouring Matters. P. KARRER (*Ber.*, 1916, **49**, 597—603. Compare Bauer, A., 1914, i, 870).—In the hope of obtaining therapeutically active substances, amino-derivatives of phenylarsinic acid have been combined with selenodiphenylamine. It is found, however, that all the selenazine dyes which have been biologically investigated have the same toxicity as the corresponding thiazine compounds, and hence are not decomposed within the organism. Numerous unsuccessful attempts have been made to prepare the selenium methylene-blue described by Cornelius and Wassermann.

3-*Phenylaminophenazselenonium chloride* (annexed formula, I) is prepared by the action of ferric chloride on an alcoholic solution of selenodiphenylamine and aniline hydrochloride. It dissolves in alcohol with a pure, green colour. 3-p-*Phenylarsinaminoselenazine* (annexed formula, II), green powder, is similarly



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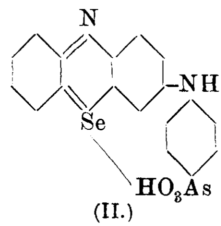
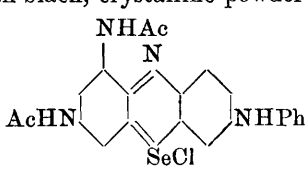


(II.)

prepared from selenodiphenylamine, sodium arsanilate, and ferric chloride.

6 : 8-*Diacetylamino*-3-*phenylaminophenazselenonium chloride*, bluish-black, crystalline powder (annexed formula, III), is obtained



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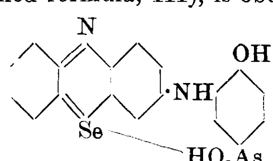


(IV.)

by acetylation of the tin double salt of 6 : 8-diaminoselenazine

(Bauer, *loc. cit.*) and oxidation of the product with ferric chloride in the presence of aniline hydrochloride.

[3-p-*Hydroxyphenylarsinamino*]-*selenazine*, green dye, which dissolves in alkalis with a reddish-violet, in water or alcohol with a green colour, is obtained from selenodiphenylamine, sodium aminohydroxyphenylarsinate, and ferric chloride (annexed formula, IV).

A modified method for the preparation of 3:6-diaminophenazselenonium chloride is described. H. W.

Dyes of the Methylene-blue Group. I. Preparation of Methylene-blue as a Lecture Experiment. F. KEHRMANN [with R. SPEITEL] (*Ber.*, 1916, **49**, 53—54).—The easy conversion of phenazthionium perbromide (A., 1915, i, 304) into the bromide of methylene-blue is well adapted to use as an experiment for lecture purposes.

A solution of 1 to 2 grams of thiodiphenylamine in acetic acid is treated at the ordinary temperature with a 5% solution of bromine in the same solvent until the primary deep green precipitate of the semi-quinonoid bromide is converted into a brownish-red, crystalline precipitate of the phenazthionium perbromide. This is separated by filtration, washed with ether, and then treated in alcoholic suspension with dimethylamine, when needles of the dye separate, the whole experiment requiring approximately ten minutes. The reaction is expressed by the equation

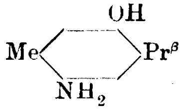
$$C_6H_4{<}{\genfrac{}{}{0pt}{}{N}{SBr}}{>}C_6H_4 + 4Br + 2NHMe_2 = NMe_2{\cdot}C_6H_3{<}{\genfrac{}{}{0pt}{}{N}{SBr}}{>}C_6H_3{\cdot}NMe_2 + 4HBr.$$

Phenazthionium perchlorate also can be used, when the crystalline perchlorate of methylene-blue is obtained, but with the other phenazthionium salts generally the yield is poor and the dye does not crystallise directly. D. F. T.

Reduction by means of Phenylhydrazine of Azo- and Bisazo-derivatives of Phenols and Aromatic Hydroxy-aldehydes. E. PUXEDDU (*Gazzetta*, 1916, **46**, i, 211—219. Compare this vol., i, 292).—Phenylhydrazine reduces hydroxyazo-compounds easily and rapidly to amino-phenols, and the azo-derivatives of hydroxy-acids to aminohydroxy-acids. The reduction of azo-derivatives of various phenols and of bisazothymol and bisazocarvacrol has now been studied. In this way benzeneazocarvacrol and benzeneazothymol are converted into the corresponding substituted aminophenols (compare Oddo and Puxeddu, A., 1905, i, 842). Bisazothymol gives an unstable, white compound, which rapidly blackens and resinifies, and is probably the diamino-derivative resulting from reduction of the two azo-groups; under other experimental conditions, however, only one of the azo-groups undergoes reduction. In the case of benzeneazosalicylaldehyde, reduction of the benzeneazo-group to the amino-residue takes place, the phenylhydrazone of the aminohydroxybenzaldehyde being obtained.

Bisazothymol forms reddish-brown, silky, flexible needles, m. p. 180—185°; Mazzara and Possetto (A., 1885, 893) gave m. p. 168°. Its *acetyl* derivative forms silky, orange needles, m. p. 145—155°.

6-*Aminothymol* (annexed formula), obtained by the action of phenylhydrazine on benzeneazothymol, forms shining, white scales, m. p. 178—179°, and yields thymoquinone on oxidation with ferric chloride.



2 : 6-Diaminothymol, formed by the reduction of bisazothymol or its acetyl derivative, was obtained only as an impure, yellowish-grey substance, decomposing at about 255°. Oxidation by means of ferric chloride converts it into a brick-red *hydroxythymoquinone*, m. p. 165°.

5-*Amino*-2-*hydroxybenzaldehydephenylhydrazone*, $C_{13}H_{13}ON_3$, obtained by the reduction of benzeneazosalicylaldehyde, forms yellow crystals, m. p. 165°. T. H. P.

Action of Hydrazine Hydrate on Nitriles. I. LIFSCHITZ (*Ber.*, 1916, **49**, 489—493. Compare A., 1915, i, 465).—A reply to Curtius, Darapsky, and Müller (this vol., i, 84). H. W.

Nitrosohydrazones and their Rearrangement. M. BUSCH and HERM. KUNDER (*Ber.*, 1916, **49**, 317—334).—The question whether nitrosoaldehydehydrazones have the constitution NO·NR·N:CHR or NHR·N:CR·NO, was answered by Bamberger and Pemsel in favour of the second formulation (compare A., 1903, i, 283—286), because these compounds are rearranged by pyridine into azoaldoximes and oxidised by amyl nitrite to nitroformaldehydehydrazones. They attempted to disprove the possibility of the nitrosoamine structure being the correct one, and that rearrangement into the other form may precede the above reactions, but the present authors are now able to show that this is indeed the case. The behaviour of ketohydrazones towards nitrous acid has also been studied, and the evidence obtained supports the view that the nitrosohydrazones are nitrosoamines.

If benzaldehydephenylhydrazone is treated with a nitrite in acetic acid solution, it is converted into the nitrosoamine,

NO·NPh·N:CHPh,

which is a viscous, brownish-yellow oil. The ethereal solutions of the oil gradually deposit diphenyldibenzylidenehydrotetrazine, and then become dark red and change into solutions of phenylnitroformaldehydephenylhydrazone, $NHPh\cdot N{:}CPh\cdot NO_2$. Benzaldehydephenylmethylhydrazone, $C_6H_5\cdot NMe\cdot N{:}CHPh$, having no imino-group, is not affected by nitrous acid under these conditions. Benzaldehyde-*p*-bromophenylhydrazone, however, yields the *nitrosoamine*, $C_6H_4Br\cdot N(NO)\cdot N{:}CHPh$, in slender, yellow needles, m. p. 68—69° (decomp.), and this changes into the red compound, $C_6H_4Br\cdot NH\cdot N{:}CPh\cdot NO_2$, when left in benzene solution.

Benzophenonephenylhydrazone yields the *nitrosoamine*,

$NO\cdot NPh\cdot N{:}CPh_2$,

in glistening, lemon-yellow needles or columns, m. p. 105°

(decomp.). Like the other nitrosoamines, this gives the Liebermann reaction. The hydrazone is regained when the compound is treated with alcoholic potassium hydroxide or zinc dust and acetic acid, or even when boiled with benzene, but in cold benzene solutions it gradually changes into benzophenone-*p*-nitrophenylhydrazone, $NO_2\cdot C_6H_4\cdot NH\cdot N\!:\!CPh_2$. If an ethereal solution of the nitrosoamine is left with a trace of hydrogen chloride, there is also formed the *o*-nitrophenylhydrazone, whilst in alcohol the rearrangement leads to a mixture of *o*- and *p*-nitro- and 2:4-dinitrophenylhydrazones. This wandering of the nitroso-group into the benzene ring, accompanied by oxidation, was not expected, and it was not until the reduction of the product (subsequently recognised as the *p*-nitrophenylhydrazone) was studied that the process could be understood. Reduction with zinc dust and acetic acid yields *benzophenone-*p*-aminophenylhydrazone*,

$$NH_2\cdot C_6H_4\cdot NH\cdot N\!:\!CPh_2,$$

in pale yellow leaflets, m. p. 166—167°, which gives the following derivatives: *hydrochloride*, glistening, grey leaflets, m. p. 215—216°; *platinichloride*, pale yellow needles; *acetyl* compound, clusters of pale brown needles, m. p. 204°; *aminoazo-dye*,

$$CPh_2\!:\!N\cdot NH\cdot C_6H_4\cdot N\!:\!N\cdot C_{10}H_6\cdot NH_2,$$

on diazotising and coupling with β-naphthylamine, very dark brown nodules, m. p. 203°; *benzylidene* compound,

$$CPh_2\!:\!N\cdot NH\cdot C_6H_4\cdot N\!:\!CHPh,$$

glistening spikelets, m. p. 138—139°; and *phenylthiocarbamide* derivative, $CPh_2\!:\!N\cdot NH\cdot C_6H_4\cdot NH\cdot CS\cdot NHPh$, white leaflets, m. p. 180·5°.

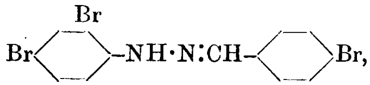
Acetophenonephenylhydrazone also yields a *nitrosoamine*, $NO\cdot NPh\cdot N\!:\!CMePh$, m. p. 82° (decomp.), which undergoes rearrangement into acetophenone-*p*-nitrophenylhydrazone when left in benzene. *Acetophenone-ψ-cumylhydrazone*, $C_{17}H_{20}N_2$, stout needles, m. p. 140—141°, forms an unstable *nitrosoamine*, in silky needles, m. p. about 70° (decomp.). *Acetophenone-*o*-iodophenylhydrazone*, stout prisms, m. p. 87°, yields a *nitrosoamine*, in yellow needles, m. p. 75° (decomp.).

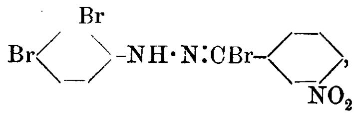
*Benzophenone-*o*-anisylhydrazone*, $C_{20}H_{18}ON_2$, thick prisms, m. p. 101°, and the vic.-*m-xylylhydrazone*, $C_{21}H_{20}N_2$, flat, silky needles, m. p. 111—112°, like other ortho-substituted arylhydrazones, react sluggishly with nitrous acid to give unstable nitrosoamines.

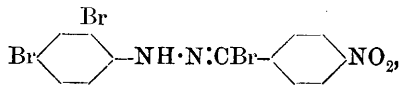
J. C. W.

Action of Bromine on Certain Hydrazones. R. Ciusa and L. Vecchiotti (*Gazzetta*, 1916, **46**, i, 240—248).—The action of bromine on the phenylhydrazones of benzaldehyde, *o*-, *m*-, and *p*-nitrobenzaldehydes, and piperonaldehyde yields the corresponding tribromo-derivatives, whereas with benzaldehydephenylmethylhydrazone a monobromo-derivative is obtained. In these tribromo-compounds two of the bromine atoms are easily shown to be in the ortho- and para-positions in the hydrazinic phenyl, since the action of bromine on the *p*-bromo- and *o*:*p*-dibromophenylhydrazones gives the same tribromo-derivatives as are obtained from the non-

brominated phenylhydrazones. With reference to the third bromine atom, it is found (1) that the tribromo-compounds obtained are not identical with the 2:4:6-tribromophenylhydrazones; (2) that, when oxidised by means of alkaline permanganate, the tribromo-derivatives of benzaldehydephenylhydrazone and of *m*- and *p*-nitrobenzaldehydephenylhydrazones yield respectively a brominated acid having the melting point of *p*-bromobenzoic acid and *m*- and *p*-nitrobenzoic acids, whilst benzaldehydephenylhydrazone gives benzoic acid. The conclusion is drawn that the tribromo-derivatives have the respective formulæ





and 

although it is possible that in the last two cases the third bromine atom may be in the unsymmetrical position in the hydrazinic phenyl group (compare Bülow and Neber, A., 1913, i, 910).

p-*Bromobenzaldehyde*-2:4-*dibromophenylhydrazone*, $C_{13}H_9N_2Br_3$, forms long, silky, white needles, m. p. 114—115°, and is given by the phenylhydrazones of both benzaldehyde and its *p*-bromo-derivative.

Benzaldehyde-2:4:6-*tribromophenylhydrazone* forms white needles, m. p. 96°.

The *tribromo*-derivative of p-*nitrobenzaldehydephenylhydrazone*, $C_{13}H_8O_2N_3Br_3$, forms silky, yellow needles, m. p. 214°, and the isomeric p-*nitrobenzaldehyde*-2:4:6-*tribromophenylhydrazone*, yellow needles, m. p. 202°.

The *tribromo*-derivative of m-*nitrobenzaldehydephenylhydrazone* forms yellow crystals, m. p. 175—176°, and the isomeric m-*nitrobenzaldehyde*-2:4:6-*tribromophenylhydrazone*, yellow needles, m. p. 172—173°.

The *tribromo*-derivative of o-*nitrobenzaldehydephenylhydrazone* forms yellow needles, exploding at 144°, and the isomeric o-*nitrobenzaldehyde*-2:4:6-*tribromophenylhydrazone*, yellow needles, m. p. 173°.

The *tribromo*-derivative of *piperonaldehydephenylhydrazone*, $C_{14}H_9O_2N_2Br_3$, forms long, white needles, m. p. 179—180°.

Benzaldehyde-p(?)-*bromophenylmethylhydrazone*, $C_{14}H_{13}N_2Br$, forms colourless plates, m. p. 104°, and yields benzaldehyde on hydrolysis. T. H. P.

The Acid-Gelatin Equilibrium. HENRY RICHARDSON PROCTER and JOHN ARTHUR WILSON (T., 1916, **109**, 307—319; compare T., 1914, **105**, 313).—Gelatin combines with acids to form highly ionisable salts analogous to the ammonium salts. From the fact that the jelly is completely permeable to all diffusible molecules

and ions concerned in the equilibrium, it follows that the product of the concentrations of any pair of diffusible and oppositely charged ions must be the same in the jelly as in the surrounding acid solution. Further, it follows that the concentration of diffusible ions in the jelly must always be greater than that in the external solution. This excess (*e*) of the ion concentration in the jelly is the measure of the difference between the osmotic pressures of the two phases. Since the anion of the gelatin salt cannot be separated from its colloid cation, the jelly mass is subjected to an outward pull which is measured by the difference *e*. Since this is uniform in all directions, the effect produced is an increase in the volume of the jelly, which is proportional to *e*.

The quantity *e* can be expressed in terms of the concentration of the acid in the outer solution and of that of the gelatin salt, giving an equation which explains the peculiarities of the curves of swelling of gelatin in acids of different concentrations and degrees of ionisation. Other formulæ have been derived which explain the difference between the action of stronger and weaker acids, as well as that of neutral salts, in repressing the swelling due to acids. The equations are said to be directly applicable to the swelling and contraction effects produced by electrolytes on colloid jellies in general. H. M. D.

The Swelling of Gelatinous Tissues. H. R. PROCTER and DONALD BURTON (*J. Soc. Chem. Ind.*, 1916, **35**, 404—409).—Mainly a summary of work which has already been published *in extenso* (T., 1914, **105**, 314). The authors further discuss the application of the theory previously developed to the actual problems of leather manufacture, particularly to the 'pickling' process. G. F. M.

Enzyme Action. K. GEORGE FALK and KANEMATSU SUGIURA (*J. Amer. Chem. Soc.*, 1916, **38**, 921—922).—The nitrogen estimations in a number of solid preparations of lipolytic enzymes previously described (compare A., 1915, i, 92) were made by Kober's aeration method, and in view of the untrustworthiness of this procedure (compare this vol., ii, 341), the nitrogen percentages have been redetermined, using the ordinary heat distillation. The new results are given and are higher than those previously recorded, and approximate more nearly to the analyses of similar substances described by Osborne (The Vegetable Proteins, 1909). W. G.

Influence of Certain Substances on the Activity of Invertase. EDWARD G. GRIFFIN and J. M. NELSON (*J. Amer. Chem. Soc.*, 1916, **38**, 722—730).—The inversion of sucrose by invertase has been studied by means of the polarimeter, the H-ion concentrations of the solutions being determined at the same time by Fales and Nelson's method (this vol., i, 174), and the effect of certain substances which have been supposed to inhibit the activity of invertase has therefore been critically examined.

Beard and Cramer (A., 1915, i, 629) showed that glass beads

inhibit the activity of lipase, diastase, and invertase, and suggested that this was due to increased surface action. It is traceable to the solubility of the glass, however, for the activity is constant if the H-ion concentration is maintained.

Eriksson (A., 1911, i, 698) found that serum neutralised with hydrochloric acid inhibited the activity of invertase, and Hedin (A., 1910, i, 290) noted that serum and egg-albumin had the same effect on rennet. They supposed that the inhibitor formed a compound with the enzyme. Here again there is no inhibition if the H-ion concentration is constant, no matter how long the invertase is in preliminary contact with the serum or albumin.

Eriksson also found that animal charcoal inhibits the activity of invertase. It is found, however, that although charcoal adsorbs the enzyme, yet the inversion of the sugar is constant if the H-ion concentration is constant. If much charcoal is used there arises the experimental difficulty of removing from it all the sugar for polarimetric observation. Aluminium hydroxide also completely removes invertase from a solution, but does not influence its activity. J. C. W.

Phosphine Sulphides and Phosphine Selenides. WILHELM STRECKER and CHARLOTTE GROSSMANN (*Ber.*, 1916, **49**, 63—87).—In extension of the work of Sauvage (A., 1904, i, 1072) on the action of phosphoryl chloride on magnesium aryl haloids, the authors have investigated the behaviour of phosphorus thiochloride towards organo-magnesium compounds. The reaction is found to be very vigorous, magnesium phenyl bromide yielding triphenylphosphine sulphide, colourless needles, m. p. 161° (Michaelis and Gleichmann, A., 1882, 1063; Michaelis and von Soden, A., 1885, 1134, give 157·5°), but only tarry products were obtained with the magnesium α- and β-naphthyl bromides. Magnesium benzyl chloride was converted into a mixture of tribenzylphosphine sulphide, m. p. 274°, identical with the product of Letts and Collie (A., 1882, 724), and *hydroxydibenzylphosphine sulphide*, $PS(CH_2Ph)_2 \cdot OH$, leaflets, m. p. 171°; the latter substance, which is feebly acid and soluble in alkalis without decomposition, owes its formation to the primary production of a monochloro-compound. The behaviour with the magnesium alkyl haloids is less simple, and a large excess of the Grignard reagent is necessary for a satisfactory result; under these conditions magnesium ethyl bromide gave *hydroxydiethylphosphine sulphide*, $PSEt_2 \cdot OH$, leaflets, m. p. 76°, probably accompanied by a small quantity of a mono-ethyl derivative. From these results it appears that Grignard reagents act on phosphorus thiochloride and phosphoryl chloride in a similar manner.

Phosphine sulphides can also be produced by the direct combination of sulphur with phosphines, and the substances obtained in this way (Michaelis and von Soden, *loc. cit.*) are identical with the compounds prepared by the Grignard reaction as described above. It is therefore almost certain that since phosphorus is indubitably quinquevalent in these organic compounds, the phosphorus thio-

chloride which gives rise to them at relatively low temperatures by the Grignard reaction must also contain quinquevalent phosphorus, and the constitution of phosphorus thiochloride is to be represented $S\colon PCl_3$ (compare Gmelin-Kraut, vol. i., **3**, 349; Thorpe, this Journal, 1875, 731). The view that phosphorus thiochloride may be an eutectic mixture of one part of phosphorus pentasulphide with three of phosphorus pentachloride (Vasilieff, A., 1910, ii, 606) is also discountenanced by these results with the Grignard reaction, because neither of the suggested constituents gives the same products.

As all endeavours to prepare phosphorus selenochloride by methods analogous to those used for phosphorus thiochloride proved fruitless, an attempt was made to prepare this substance by combining dichlorophenoxyphosphine, $PCl_2{\cdot}OPh$, with selenium, with subsequent decomposition of this substance by phosphorus pentachloride to give the selenochloride, $PSCl_3$; the first reaction, however, took another course, due to the thermal decomposition of dichlorophenoxyphosphine into phosphorus trichloride, chlorodiphenoxyphosphine, and triphenoxyphosphine below the temperature necessary for combination with selenium (compare Noack, A., 1883, 735); the product from heating together dichlorophenoxyphosphine and selenium under suitable conditions therefore included triphenoxyphosphine selenide and chlorodiphenoxyphosphine selenide.

Dichlorophenoxyphosphine combines with sulphur at 220—230° in a sealed tube with formation of dichlorophenoxyphosphine sulphide, which has already been described under the name phenyl dichlorothiophosphate (Ephraim, A., 1912, i, 26). In a similar manner chlorodiphenoxyphosphine sulphide (*hydrazide*,

$$PS(OPh)_2{\cdot}NH{\cdot}NH_2,$$

m. p. 62—63°) can be obtained by heating diphenyl chlorothiophosphate with sulphur at 200° in an open vessel, whilst by heating the diphenyl ester with selenium at 260°, *chlorodiphenoxyphosphine selenide*, $PSeCl(OPh)_2$, colourless needles, m. p. 59—59·5°, is obtained, which at 180° slowly undergoes decomposition according to the equation $3PSeCl(OPh)_2 = 2SeP(OPh)_3 + Se + PCl_3$, and is decomposed by phosphorus pentachloride with formation of selenium chloride. When treated in alcoholic solution with ammonia, and in the solid state with hydrazine hydrate, chlorodiphenoxyphosphine selenide is converted into *aminodiphenoxyphosphine selenide*, $PSe(OPt)_2{\cdot}NH_2$, crysalline scales, m. p. 78°, and *hydrazinodiphenoxyphosphine selenide*, $PSe(OPh)_2{\cdot}NH{\cdot}NH_2$, colourless needles, m. p. 68°, respectively. *Triphenoxyphosphine selenide*, $PSe(OPh)_3$, needles, m. p. 73—74°, always accompanies chlorodiphenoxyphosphine selenide when prepared in the manner described above, but it can be obtained more conveniently by heating triphenoxyphosphine with selenium at 240°.

In the light of the preceding results, it appeared possible that chlorine, on account of its strongly negative character, effected an opposition to the addition of selenium. This idea receives some support from the fact that although *dibromophenoxyphosphine*,

$PBr_2(OPh)$, an unstable liquid, b. p. 130—132°/11 mm., resembles its chlorine analogue in resisting the addition of selenium, the *bromodiphenoxyphosphine*, $PBr(OPh)_2$, a rather unstable liquid, b. p. 189—192°/11 mm., combines with selenium at 190°, giving *bromodiphenoxyphosphine selenide*, $PSe(OPh)_2Br$, colourless crystals, m. p. 64—65°, which is convertible into the hydrazide described above. Both the dibromo- and the monobromo-compounds react with sulphur, yielding respectively *dibromophenoxyphosphine sulphide*, $PSBr_2{\cdot}OPh$, a pale yellow liquid, b. p. 156—157°/11 mm., and bromodiphenoxyphosphine sulphide, $PSBr(OPh)_2$, colourless needles, m. p. 72·5°.

In order to examine the effect of variation of the organic radicles on the reactivity of the substituted phosphine towards sulphur and selenium, other compounds of this type were prepared. *Dichloro*-p-*tolyloxyphosphine*, $PCl_2{\cdot}O{\cdot}C_6H_4Me$, a mobile liquid, b. p. 118°/11 mm., *chlorodi*-p-*tolyloxyphosphine*, $PCl(O{\cdot}C_6H_4Me)_2$, b. p. 206—208°/11 mm., and *tri*-p-*tolyloxyphosphine*, $P(O{\cdot}C_6H_4Me)_3$, a pale yellow, viscous oil, b. p. 285°/11 mm., were obtained by the interaction of phosphorus trichloride and *p*-cresol. The first-named product reacted with sulphur at 220°, giving *dichloro*-p-*tolyloxyphosphine sulphide*, $PSCl_2{\cdot}O{\cdot}C_6H_4Me$, b. p. 135—136°/11 mm.; the second product reacted with sulphur at 180° and with selenium at 200°, giving respectively chlorodi-*p*-tolyloxyphosphine sulphide, $PSCl(O{\cdot}C_6H_4Me)_2$, m. p. 54—55° (*hydrazide*, m. p. 141°; compare Autenrieth and Hildebrand, A., 1898, i, 419), and *chlorodi*-p-*tolyloxyphosphine selenide*, $PSeCl(O{\cdot}C_6H_4Me)_2$, colourless needles, m. p. 48—49° (*hydrazide*, needles, m. p. 106—108°); the third compound united with sulphur at 140—150° and selenium at 170°, yielding respectively *tri*-p-*tolyloxyphosphine sulphide*, $PS(O{\cdot}C_6H_4Me)_3$, colourless needles, m. p. 93—94°, and *tri*-p-*tolyloxyphosphine selenide*, $PSe(O{\cdot}C_6H_4Me)_3$, colourless needles, m. p. 111—112°.

The corresponding *o*-tolyloxy-compounds were prepared in a similar manner. *Dichloro*-o-*tolyloxyphosphine*, a colourless, fuming liquid, b. p. 116°/11 mm.; *dichloro*-o-*tolyloxyphosphine sulphide*, b. p. 130—131°/15 mm. *Chlorodi*-o-*tolyloxyphosphine*, b. p. 195—196°/11 mm.; *chlorodi*-o-*tolyloxyphosphine sulphide*, b. p. 130—131°/15 mm.; *chlorodi*-o-*tolyloxyphosphine selenide*, b. p. 224—227°/11 mm. (*hydrazide*, m. p. 98—99°). *Tri*-o-*tolyloxyphosphine*, viscous, pale yellow oil, b. p. 248°/11 mm (slight decomp.); *tri*-o-*tolyloxyphosphine sulphide*, needles, m. p. 45—46°, b. p. 280—290°/11 mm.; *tri*-o-*tolyloxyphosphine selenide*, colourless needles, m. p. 50—51°.

The following compounds also are described: *dichloro*-p-*chlorophenoxyphosphine*, $PCl_2{\cdot}O{\cdot}C_6H_4Cl$, b. p. 128—130°/12 mm.; *dichloro*-p-*chlorophenoxyphosphine sulphide*, $PSCl_2{\cdot}O{\cdot}C_6H_4Cl$, b. p. 143—145°; *dichloro*-p-*chlorophenoxyphosphine selenide*,

$$PSeCl_2{\cdot}O{\cdot}C_6H_4Cl,$$

crystals, m. p. 59—61°, b. p. 245—255°/11 mm. *Chlorodi*-p-*chlorophenoxyphosphine*, $PCl(O{\cdot}C_6H_4Cl)_2$, b. p. 225—227°/11 mm.; chlorodi-*p*-chlorophenoxyphosphine sulphide, $PSCl(O{\cdot}C_6H_4Cl)_2$, m. p. 43—44°, b. p. 243—245°/11 mm. (compare Autenrieth and

Hildebrand, *loc. cit.*, who give m. p. 92°); *chlorodi*-p-*chlorophenoxyphosphine selenide*, $PSeCl(O\cdot C_6H_4Cl)_2$, m. p. 59—61°, b. p. 245—255°/11 mm. Tri-*p*-chlorophenoxyphosphine sulphide, $SP(O\cdot C_6H_4Cl)_3$, needles, m. p. 85—86°; Autenrieth and Hildebrand obtained tablets, m. p. 113—114°, but the lower result was independently confirmed by the present authors, who also obtained the compound, m. p. 85—86°, by replacing the selenium in tri-*p*-chlorophenoxyphosphine selenide (Michaelis, A., 1898, 417) by sulphur. *Tri*-p-*nitrophenoxyphosphine*, $P(O\cdot C_6H_4\cdot NO_2)_3$, colourless needles, m. p. 170—171°, decomposes vigorously a little above its m. p., and so was unsuited to additive reactions with sulphur or selenium.

No additive reactions of the above type were discovered with tellurium. D. F. T.

New Heterocyclic Systems. II. Pyrrolidine Analogues, in which the Nitrogen Atom is Replaced by Phosphorus, Arsenic, or Antimony. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1916, **49**, 437—444. Compare this vol., i, 92).—Just as the dichloroarylphosphines, etc., react with the magnesium compound of $\alpha\epsilon$-dibromopentane to form analogues of piperidine, so they react with the $\alpha\delta$-dibromobutane salt, with even greater ease, to form 5-ring systems. The phosphorus and arsenic atoms in these compounds seem to possess residual affinities to a remarkable extent, for additive compounds with many solvents, inorganic haloids, etc., have been obtained. These will be described later.

The magnesium compound of $\alpha\delta$-dibromobutane was treated with phosphenyl chloride in cold ether, and, after removing the solvent, the dry residue was distilled in a current of hydrogen under 20 mm. The distillate, bath up to 350°, was fractionated, and yielded about equal amounts of an oil, b. p. 135—145°/18 mm., and a residue of high boiling point. The former consisted of *phenyl*cyclo*tetramethylenephosphine*, $C_4H_8{:}PPh$, a colourless oil with powerful odour of phosphine, which was only slowly oxidised by the air, but energetically by silver nitrate; b. p. 132—133°/16—18 mm., $D_4^{22\cdot5}$ 1·0335, $n_D^{22\cdot5}$ 1·5894. The base formed a *mercurichloride*, $C_{10}H_{13}P,HgCl_2$, in highly refractive rhombohedra, m. p. 143—144° (decomp.), and gave other phosphonium salts when treated with alkyl iodides; *ethiodide*, pale yellow, crystalline powder, m. p. 122°; n-*propiodide*, a light, white powder, m. p. 153—154°; iso*propiodide*, pale yellow.

Phenyldichloroarsine was applied in the same way, and *phenyl*cyclo*tetramethylenearsine*, $C_4H_8{:}AsPh$, was obtained as a colourless, mobile oil, with faint, not unpleasant odour; b. p. 128·5°/15—16 mm. (corr.), D_4^{17} 1·2824, n_D^{17} 1·6768. This gave the following arsonium salts: *dichloride*, $C_{10}H_{13}AsCl_2$, very hygroscopic, snow-like crystals, m. p. 120·5°; *mercurichloride*, $C_{10}H_{13}As,HgCl_2$, hexagonal leaflets, m. p. 160—162°; *methiodide*, $C_{10}H_{13}As,MeI$, m. p. 135—136°; *ethiodide*, pale yellow, m. p. 85—86°; n-*propiodide*, slender, white needles, m. p. 123—124°; iso*propiodide*, m. p. 113—114°.

*Phenyl*cyclo*tetramethylenestibine*, $C_4H_8\colon SbPh$, was also prepared from phenyldichlorostibine. It formed an unpleasant-smelling, colourless oil, b. p. 156—158°/20—22 mm., n_D^{23} 1·6313, and yielded a *dichloride*, doubly refractive, white lozenges, m. p. 150°, and a *dibromide*, stellar aggregates of doubly refractive needles, m. p. 149°.

Residues of high-boiling point were obtained in considerable quantities in each synthesis. They were found to have high molecular weights and to combine vigorously with bromine, alkyl iodides, or mercuric chloride. J. C. W.

Electrochemical Experiments with Organic Arsenic Compounds. FR. FICHTER and EPHRAIM ELKIND (*Ber.*, 1916, **49**, 239—250).—The authors have investigated the electrolytic oxidation and reduction of arsenic compounds along the lines followed in the case of sulphur compounds (1907—1915). Many reductions of arsenic compounds had already been effected by electrochemical methods, but no oxidations.

The influence of various factors was investigated first in the case of *p*-aminophenylarsinic acid. This and other arsinic acids are not affected by electrolytic hydrogen except in an acid medium, and then yields *p*-aminophenylarsine if air is excluded or *p*-arsenoaniline if this is not done; thus,

$$NH_2\cdot C_6H_4\cdot AsO_3H_2 \longrightarrow NH_2\cdot C_6H_4\cdot AsO \longrightarrow NH_2\cdot C_6H_4\cdot AsH_2 \longrightarrow (NH_2\cdot C_6H_4)_2As_2.$$

In a solution containing an excess of a mineral acid ("catolyte," approximately a 10% solution in $2N$-HCl, "anolyte," $2N$-HCl) the most effective cathode is found to be amalgamated zinc, closely followed by mercury and amalgamated lead. Increasing the current density is only effective in the case of a lead cathode. Since *p*-aminophenylarsine hydrochloride is insoluble in acids of more than $2N$-concentration, it is better to use an aqueous-alcoholic acid; this allows of using more acid, and so preventing any loss of the free base, and the improvement is very marked in the case of lead and amalgamated lead cathodes. Sulphuric acid is not a suitable solvent, as *p*-aminophenylarsine sulphate is almost insoluble. The temperature must be kept low, otherwise aniline and arsenious acid, or even arsine, are formed, thus;

$$NH_2\cdot C_6H_4\cdot AsO_3H_2 + H_2 = C_6H_5\cdot NH_2 + H_3AsO_3.$$

p-Aminophenylarsine is described as an oil, b. p. 133·5°/13 mm., and the hydrochloride and sulphate as white, crystalline powders (compare Kahn, *Chem. Zeit.*, 1912, **36**, 1099).

The above reduction involves the reduction of *p*-aminophenylarsenoxide (as indicated). If this is reduced alone it yields a solution of *p*-aminophenylarsine hydrochloride with a mercury cathode in an acid solution, but a precipitate of *p*-arsenoaniline with other cathodes, especially in an alkaline medium. Two reactions are indicated, thus: $NH_2\cdot C_6H_4\cdot AsO + 2H_2 = H_2O + NH_2\cdot C_6H_4\cdot AsH_2$, and this $+ NH_2\cdot C_6H_4\cdot AsO = (NH_2\cdot C_6H_4)_2As_2 + H_2O$. For this reduction lead cathodes are most efficient. Bart (A., 1914, i, 761) has patented the process, but gave no details.

Phenylarsinic acid is reduced in aqueous-alcoholic hydrochloric acid to the non-basic phenylarsine, b. p. 55°/14 mm. (Palmer and Dehn, A., 1902, i, 86, and Kahn, *loc. cit.*).

o-Nitrophenylarsinic acid (Bart, A., 1913, i, 115) is reduced in a solution in 2*N*-sodium acetate at a water-cooled platinum cathode to *hydrazobenzene-2:6-diarsinic acid*, $(C_6H_4 \cdot AsO_3H_2)_2N_2H_2$, a pale brown powder, whereas both the nitro- and arsinic acid groups are completely reduced in an acid solution at a lead cathode.

Dehn (A., 1908, i, 720), who reduced cacodyl chloride, did not succeed in reducing cacodylic acid. This is possible, however, at an amalgamated zinc cathode in 2*N*-sulphuric acid, the main product being cacodyl, only a little dimethylarsine being observed, thus: $Me_2AsO_2H \longrightarrow As_2Me_4 \longrightarrow AsHMe_2$.

Cacodylic acid is partly oxidised at a platinum anode in an alkaline solution to carbon dioxide and arsenic acid. From an estimation of these products (precipitating the arsenic acid with magnesium mixture in the cold) it became obvious to the authors that methylarsinic acid must also have been formed, for more than four times as much carbon dioxide was observed as was expected. Search was made for this acid, and it was precipitated as the magnesium salt in one experiment on warming the filtrate from the magnesium ammonium arsenate (compare Dehn, A., 1905, i, 184).

The electric conductivities of phenylarsinic, *p*-aminophenylarsinic, and *o*-nitrophenylarsinic acids were measured at 25°. The mean values of K are 0·11, 0·028, and 0·17 respectively.

J. C. W.

Derivatives of *p*-Dimethylaminophenylarsinic Acid. LES ETABLISSEMENTS POULENC FRÈRES (Eng. Pat., 1914, 22521; from *J. Soc. Chem. Ind.*, 1916, **35**, 437).—*p*-Dimethylaminophenylarsinic acid gives on nitration with a mixture of nitric acid, or an alkali nitrate, with sulphuric acid, according to conditions, either *2-nitro-1-dimethylaminophenyl-4-arsinic acid*, or a mixture of this with 4-methylnitrosoaminophenylarsinic acid, or a mixture of two dinitro-derivatives. The mononitro-compound on treatment with alkali and subsequent reduction gives 3:3′-diamino-4:4′-dihydroxyarsenobenzene (salvarsan), which is thus obtained by a simpler process than that hitherto employed. G. F. M.

Manufacture of *p*-Hydroxyphenylarsinic Acid. F. W. KAY (Eng. Pat., 1915, 6322; from *J. Soc. Chem. Ind.*, 1916, **35**, 437). —The acid is obtained as a syrupy solution by the method described in D.R.-P. 205616 (A., 1909, i, 279), and is purified by means of its readily crystallisable sodium salt. G. F. M.

Preparation of *m*-Amino-*p*-hydroxyphenylarsinic Acid. A. MOUNEYRAT (Eng. Pat., 1915, 3087; from *J. Soc. Chem. Ind.*, 1916, **35**, 437).—*m*-Amino-*p*-hydroxyphenylarsinic acid is obtained from its corresponding nitro-compound by electrolytic reduction in a double cell, using 2 amperes at 3·5—4 volts, with a mercury

cathode and a nickel anode immersed in sodium hydroxide solution in the inner cell. The nitro-compound dissolved in a large excess of hydroxide is placed over the mercury in the outer cell.

G. F. M.

Preparation of Complex Arseno-compounds. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Eng. Pat., 1915, 17482; from *J. Soc. Chem. Ind.*, 1916, **35**, 489).—The hydrochloride of a new complex arseno-compound of unknown constitution is obtained when a solution of the hydrochlorides of 3 : 4 : 5 : 3′ : 4′ : 5′-hexa-amino-arsenobenzene, or a derivative, and of 3 : 3′-diamino-4 : 4′-dihydroxy-arsenobenzene is heated at 80°, or is kept for some time and then poured into a large excess of glacial acetic acid. The new compound differs from the parent substances in its solubility in sodium hydroxide and carbonate solutions. It has valuable therapeutic properties.

G. F. M.

Mixed Lead Tetra-aryls. KARL LEDERER (*Ber.*, 1916, **49**, 349—350).—*Lead diphenyldi*-o-*tolyl*, $PbPh_2(C_6H_4Me)_2$, has been obtained by the action of lead diphenyldi-iodide on magnesium *o*-tolyl bromide, and forms white needles, m. p. 134—135° (compare Grüttner, A., 1915, i, 334).

J. C. W.

Preparation of Mercurial Quinoline Derivatives. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P., 289246; from *J. Soc. Chem. Ind.*, 1916, **35**, 438).—Derivatives of quinoline containing one or more acidic groups, either mixed with mercury compounds, or in the form of their mercury salts, are heated until the mercury–quinoline compound becomes soluble in alkali; they are thus converted into solid mercurial compounds, which by suitable choice of the substituent groups in the quinoline may be graded with regard to their decomposition in the organism. As examples, hydroxymercuri-8-hydroxyquinoline-5-sulphonic acid, hydroxymercuri-2-phenylquinoline-4-carboxylic acid, and numerous others are mentioned.

G. F. M.

Physiological Chemistry.

Physico-chemical Investigations on Animal Liquids. X. Variation of the Refractive Index of Blood Serum during Dialysis. G. QUAGLIARIELLO and G. BECCHINI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 354—359. Compare Bottazzi, Buglia, and Jappelli, A., 1908, ii, 870).—The changes gradually occurring in ox blood-serum when the latter is dialysed into water were followed by periodic refractometric measurements and weighings of the

liquid in the dialyser. After the end of the first day, by which time the concentration of the electrolyte has been reduced in the ratio 1 :0.091, the increase in weight of the liquid is considered to depend principally on the osmotic pressure of the colloidal substances alone. By the sixteenth day the osmotic pressure of the colloidal substances of the serum is about one-sixth of the initial value, the daily diminution being subsequently virtually constant. Such marked diminution cannot be due, in more than small part, to the precipitation of insoluble globulin, since the latter constitutes not more than 9% of the total protein, and it is therefore to be attributed to a pronounced decrease in the condition of dissociation of the proteins. The whole of the reduction of the osmotic pressure is not, however, explainable in this way, and the conclusion is drawn that a new phase is formed in the liquid, consisting of more or less large aggregates of colloidal molecules, that is, of complexes which do not contribute to the osmotic pressure of the solution. This conclusion is confirmed by the variations in the refractive index. T. H. P.

The Osmotic Equilibrium between Blood and Milk. II. F. H. VAN DER LAAN (*Biochem. Zeitsch.*, 1916, **73**, 313—325).—The osmotic equilibrium between blood and milk in the cow is not disturbed in diseases of general character, even in cases where there is a change in the concentration in the blood. Diseases of the udder exert no action on the depression of the freezing point of milk; when increased depression has been noted by other authors, this is due to matter which has not been secreted, to pus, bacterial action, etc. The freezing point of the cream is identical with that of skimmed milk. The true secretion product of the milk glands has never a smaller depression than 0·53°. S. B. S.

Content of Cholesterol and Fatty Substances in the Blood. FRANK A. CSONKA (*J. Biol. Chem.*, 1916, **24**, 431—438).—See this vol., ii, **349**.

Fibrin in its Relation to Problems of Biology and Colloid Chemistry; the Problem of Blood Coagulation. VI. The Physical Methods of Fibrin Separation and Gel Formation in Fluids which Clot, which occur Naturally or have been Artificially Produced. E. HEKMA (*Biochem. Zeitsch.*, 1916, **73**, 370—427. Compare **A.**, **1914**, i, 754, 895, 1013).—A very detailed account is given of the microscopic appearances observed on the production of the fibrin clot, either from natural solutions (fluoride plasma) or such as have been made artificially, such as the alkali hydrosol described by the author. The first indication of the clot formation is the appearance of elongated ultramicrons; the fibrin in them appears in the form of needle-like bodies, which by juxtaposition can grow into fibres. Fibrin threads can also be seen to separate from the fluids without intermediate stages being visible. S. B. S.

Fibrin in its Relation to Problems of Biology and Colloid Chemistry; the Problem of Blood Coagulation. VIII. The Similarity of the Fibrin Separation to a Crystallisation Process on the One Hand, and to a Precipitation of Colloids on the Other Hand; the General Nature of the Process of Fibrin Clotting. E. HEKMA (*Biochem. Zeitsch.*, 1916, **73**, 428—449).—The fibrin clotting is assumed to take place in two phases. In the first phase the emulsoid colloid (hydrosol) is converted into a suspensoid form. The particles of fibrin first appear in the form of ultramicrons and microns in needle form. The second phase consists in the juxtaposition of these smaller elements until visible fibres are produced. Where such visible fibres are produced immediately (see preceding abstract), it is assumed that the processes of the two phases are taking place simultaneously. S. B. S.

The Phenomena of Clot Formations. III. Further Investigations of the Cholate Gel. S. B. SCHRYVER (*Proc. Roy. Soc.*, 1916, [*B*], **89**, 176—183. Compare A., 1914, i, 616).—It is shown that there is marked similarity between certain vital activities of the cell and the behaviour of the cholate gel. The erosive action of certain organic substances on the gel runs parallel with their narcotic and cytolytic actions. The gel formation by calcium chloride is inhibited by the presence of sodium, potassium, magnesium, and other chlorides. These chlorides also cause erosion of the formed gel, but the erosive action can be antagonised by the addition of relatively small amounts of calcium salts. To explain the parallelism between certain biological actions of organic substances and the antagonistic action of inorganic salts on the one hand and the action of these substances on the cholate gel on the other hand, it is suggested that the cell membrane or cytoplasm is constituted by a heterogeneous system of lipoids, proteins, etc., held together in a magma containing a gel-forming substance with similar properties to those of the cholate gel. S. B. S.

Action of Glycerol. I. Hæmolytic Action of Glycerol in Vivo and in Vitro. ITALO SIMON (*Chem. Zentr.*, 1916, i, 25; from *Arch. Farm. sperim.*, 1915, **20**, 120—128).—The blood of bullocks and of rabbits is hæmolysed by glycerol in all concentrations. The time required for hæmolysis increases with the concentration of the glycerol solution up to a certain point (55% with bullocks' blood and 50% with rabbits' blood), whilst with further increase in concentration the rate of hæmolysis rapidly increases.

Subcutaneous injections of glycerol produce serious local and general poisoning in rabbits. When the amount of glycerol exceeds 2·5 grams per kilo, hæmoglobinuria results; the concentration of the glycerol makes no difference. N. H. J. M.

Influence of Phosphates in the Intra-gastric Amylolysis. JEAN EFFRONT (*Mon. Sci.*, 1916, [v], **6**, 49—53. Compare this vol., i, 298).—The author has endeavoured to verify the results obtained *in vitro* (*loc. cit.*) by a study of the stomach contents withdrawn

during the first phases of digestion. The results obtained to a large extent confirm the deductions previously drawn, but it must be remembered that the rôle of the phosphate is not restricted to the gastric amylolysis, this factor also intervening to a very considerable extent in pancreatic amylolysis. Intra-gastric salivary digestion is normally checked at the end of fifteen minutes, and during this phase of the digestion 50—80% of the starch fed is dissolved. The phosphate present lessens the gastric secretion at the commencement of the digestion and neutralises the free acid, but in the later stages the phosphate excites the secretion and brings up the acidity to normal. W. G.

Colorimetric Method for the Estimation of Amino-acid α-Nitrogen. II. Application to the Hydrolysis of Proteins by Pancreatic Enzymes. VICTOR JOHN HARDING and REGINALD M. MACLEAN (*J. Biol. Chem.*, 1916, **24**, 503—517. Compare A., 1915, ii, 382).—The new method has been applied to the study of the action of pancreatic enzymes on serum-albumin and -globulin, gluten, fibrin, gelatin, caseinogen, nucleoprotein, and peptones, with results similar to those obtained by the van Slyke and Sörensen methods. It is claimed that the new method is the most sensitive, but is inapplicable in strongly acid or alkaline solutions.

H. W. B.

Indispensability of Lipoids for Life. WILHELM STEPP (*Zeitsch. Biol.*, 1916, **66**, 365—386. Compare A., 1913, i, 1409).—The author describes the results of further feeding experiments on white mice, which confirm those previously recorded.

The addition of pure lipoids (lecithin, kephalin, cerebrone, cholesterol), together with a vitamine preparation (orypan), to alcohol-extracted dog biscuits furnishes a food which is capable of maintaining white mice in health for more than sixty days. Neither lipoids nor vitamines are sufficient by themselves to render the alcohol-extracted biscuits adequate for the maintenance of life. In contradistinction to what has been observed with vitamines, lipoids must be taken by the mouth, parenteral administration being ineffective. H. W. B.

The Effects of Commercial Dextrose when Fed to White Rats. A. J. CARLSON, L. HEKTOEN and E. R. LE COUNT (*J. Amer. Chem. Soc.*, 1916, **38**, 930—936).—Groups of twenty-five rats were fed on a diet of carrots and unleavened white bread, and on this diet plus commercial dextrose or granulated sucrose respectively over a period of six months. Each group was weighed every fortnight, and any rats that died were subjected to gross and to microscopic examination, and at the end of the period all the surviving animals were killed and examined. Two rats in each group were the subjects of anti-substance experiments, receiving an abdominal injection of a 10% suspension of sheep's blood half-way through the period and being killed six days afterwards. The results show that the addition of commercial dextrose to the extent of 2·5—3·5 grams per kilo. of body-weight per day to the diet of white rats for a

period of six months has no abnormal influence on the animals either as regards rate of growth, fecundity, immunity reactions, or the conditions of the organs. The number of deaths from pneumonic infection or rat typhoid were about the same in each group.

W. G.

Fat Assimilation. W. R. BLOOR (*J. Biol. Chem.*, 1916, **24**, 447—460).—The author has estimated the total fat, lecithin (phosphatides), and cholesterol in the whole blood, the plasma, and (by calculation) the corpuscles during a series of fat-absorption experiments, with the following results: (1) there is a great increase in the amount of lecithin in the corpuscles during fat absorption; (2) the total fatty acids increase in both plasma and corpuscles, but the increase is generally more marked in the corpuscles, the relation between lecithin and total fatty acid in the whole blood and the corpuscles being fairly constant; (3) the amount of cholesterol remains unchanged.

The conclusions drawn from these results are: (*a*) that the corpuscles of the blood take up the absorbed fat from the plasma and transform it into lecithin; (*b*) that most, if not all, of the absorbed fat undergoes this transformation; and therefore (*c*) that lecithin is an intermediate step in the metabolism of the fats.

H. W. B.

Enzymic Scission of Polypeptides by the Action of Extracts of Animal Tissues or Organs. II. A. CLEMENTI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 234—236. Compare this vol., i, 299).—Even in small proportions, *dl*-leucylglycine, leucine, or glycine exhibits the property of determining flocculation and coagulation in moderately dilute aqueous extracts of the livers of various animals.

T. H. P.

Permeability of Cells. VI. New Method for Investigating the Permeability of the Cells of Various Regions of the Kidney by the Aid of Dyes. S. GERZOWITSCH (*Zeitsch. Biol.*, 1916, **66**, 391—410).—The anatomy of the frog allows of the independent perfusion of the glomeruli and of the urinary tubules of the kidney. The author has carried out these independent perfusions with solutions containing various dyes with and without diuretics, and has noted the rate and the extent of appearance of the dyes in the urine. The results indicate that the cells in both regions have usually the same permeability, although differences may be sometimes observed. Increased activity of the kidney cells under the stimulating influence of a diuretic is accompanied by an increased elimination of the dye; the permeability of the kidney cells for dyes is therefore a function of their state of activity.

H. W. B.

The Chemistry of Muscles. IX. I. Inorganic and Organic Phosphorus of Smooth and Striated Muscular Tissue of Birds. II. The Formation of Phosphoric Acid by Autolysis of the Muscular Tissue of Birds. A. COSTATINO (*Chem. Zentr.*, 1916, i, 375—376; from *Arch. Farm. sperim.*, 1915, **20**, 276—302).—I. A

general comparison of the distribution of phosphorus in various kinds of muscular tissue was made in the case of the fowl. The total phosphorus and soluble phosphorus of striated muscle of the bird are higher than those of the mammalian tissue. In all kinds of the muscular tissue the amount of inorganic phosphorus is greater than that of the soluble organic phosphorus. The composition of red striated muscle as regards phosphorus is intermediate between that of the white striated and smooth muscles. The total phosphorus of striated muscle is greater than that of the smooth, the red and white containing about the same amount; this remark refers more especially to the soluble and inorganic phosphorus. The phosphatide nitrogen is contained in the greatest quantity in smooth muscles. In all kinds of muscular tissue there is a considerable amount of phosphorus in organic combination. In striated muscles the amount of the acid radicles (Cl, P, etc.) is greater than that of the basic (K, Na), whereas the reverse is the case in smooth muscles; this indicates that in the latter case part of the alkali metals are combined with organic acids.

II. Phosphoric acid formed by autolysis is derived from the soluble organic phosphorus compounds and not from the phosphatides. S. B. S.

The Chemistry of Muscles. X. Chemistry of Phosphorus Compounds in Smooth Mammalian Muscle. A. Costatino (*Chem. Zentr.*, 1916, i, 376; from *Arch. Farm. sperim.*, 1915, **20**, 361—370).—By the method of Plimmer and Kaya, it is shown that the organic phosphorus compounds are nucleoproteins and not phosphoproteins, as the scission of phosphoric acid does not take place on treatment with 1% sodium hydroxide solution. Part of the nucleoprotein is soluble in 0·9% sodium chloride solution. The phosphorus content of the nucleoprotein constituent of plain muscle is about ten times as great as that of the striated muscle. S. B. S.

Arginase. IV. Antonino Clementi (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 366—368).—Examination of two human embryos, respectively four and six months old, exhibited the presence of arginase in each case (compare A., 1915, i, 606). T. H. P.

Origin of the Nitrates in the Urine. H. H. Mitchell, H. A. Shonle, and H. S. Grindley (*J. Biol. Chem.*, 1916, **24**, 461—490). —The results of a number of feeding experiments on men and pigs indicate that the animal organism may excrete in the urine more nitrate than is ingested in the food. Moreover, ingested nitrates are partly destroyed or transformed while passing through the body. The animal organism, therefore, is able to oxidise nitrogen or its compounds to nitrates. The origin of the nitrates thus produced is not known. H. W. B.

Dietary Factors Operating in the Production of Polyneuritis. E. V. McCollum and Cornelia Kennedy (*J. Biol. Chem.*, 1916, **24**, 491—502. Compare McCollum and Davis, this vol., i, 184).— In the previous papers (*loc. cit.*) it has been shown that two

accessory factors—a fat-soluble *A* and a water-soluble *B*—are indispensable in the diet if growth is to occur. The data now presented show that in the production of polyneuritis in birds by exclusive rice feeding or exclusive feeding of a ration made up of purified foodstuffs, the characteristic degeneration of the nerve cells is the specific result of a lack of the water-soluble *B*.

Pigeons which have become polyneuritic through exclusive feeding with polished rice are rapidly and completely cured if an aqueous extract of wheat or oats is added to the diet. An aqueous extract of wheat germ which has been freed previously from lipoids by exhaustion with ether, followed by carbon tetrachloride, exerts a similar curative effect. Success also attends the administration to polyneuritic birds of such substances as cabbage or potato juice, both of which are practically free from lipoids.

The accessory factor termed "water-soluble *B*" is also soluble in acetone, ethyl acetate, and benzene, and extracts made with these solvents of wheat germ, previously rendered free from fat by extraction with ether, are as effective as the aqueous extract in relieving the symptoms of polyneuritis in pigeons. H. W. B.

The Distribution and Fate of Colloidal Silver in the Mammalian Body. IV. J. Voigt (*Biochem. Zeitsch.*, 1916, **73**, 211—235).—A detailed description is given of histological preparations of the organs of animals to which colloidal silver preparations have been administered, either intramuscularly or intraperitoneally. The author draws the conclusion that it is not possible satisfactorily to protect a silver hydrosol against flocculation in the body. When injected into the peritoneum or muscles, a considerable part of the silver is precipitated at the point of injection. After intravenous injection, however, an appreciable part of the silver is carried by the blood serum to the organs, and is deposited chiefly in the liver, spleen, and bone-marrow; from these positions it is slowly removed after undergoing some change. S. B. S.

The Oligodynamic Action of Copper. K. Spiro (*Chem. Zentr.*, 1916, i, 260; from *Münch. med. Woch.*, 1915, **62**, 1601—1604).—A theoretical explanation is given of the differences between the oligodynamic and specific actions of copper. In principle, there is little difference between the two actions. S. B. S.

Antagonistic Action between Hydrogen Sulphide and Salts of Heavy Metals. Rudolfo Menegazzi (*Chem. Zentr.*, 1916, i, 25; from *Arch. Farm. sperim.*, 1915, **20**, 67—82).—Salts of heavy metals, such as mercuric chloride, copper sulphate, and lead acetate, when precipitated by hydrogen sulphide in a colloidal state from solutions containing peptone, egg-albumin, or starch can be given to dogs and rabbits in relatively large amounts without injurious results. The sulphide is changed from the sol to the gel condition. N. H. J. M.

Influence of Nitrogen Metabolism of Lævorotatory and Synthetic Glycerophosphate Subcutaneously Injected. PIETRO MONTUSCHI (*Chem. Zentr.*, 1916, i, 24; from *Arch. Farm. sperim.*, 1915, **20**, 29—37).—Lævorotatory sodium glycerophosphate injected subcutaneously slightly increased the excretion of urine by rabbits; the synthetic salt had a greater effect. The feeding is improved by both preparations. N. H. J. M.

Behaviour of Gluconic Acid in the Organism. CESARE PADERI (*Chem. Zentr.*, 1916, i, 27—28; from *Arch. Farm. sperim.*, 1915, **20**, 82—96).—Gluconic acid is not decomposed by blood or by pancreas, but is partly reduced by liver.

Subcutaneous injection of sodium gluconate produces more or less irritation, according to the amount employed. When consumed, gluconic acid is in part excreted, whilst the portion which is retained is presumably reduced to dextrose. The methods employed for detecting the different substances concerned are described. N. H. J. M.

Pharmacological Investigations of the Surviving Intestine. RICHARD MEISSNER (*Biochem. Zeitsch.*, 1916, **73**, 236—259).—There is no marked distinction between the action on the surviving intestine of those opium alkaloids which are phenanthrene derivatives and those which are *iso*quinoline derivatives. The phenanthrene alkaloids do not behave in the same way towards the small intestine, although the action is generally a paralytic one. If the substances under investigation are brought into the inside of the intestine, the action produced is the same as that produced when applied in the usual manner, although it is demonstrated somewhat later. The action of a large number of plant extracts on the isolated intestine was tested, and was found to be not always parallel with its action on the intestine of the living subject; some extracts which excite the intestine of the living subject paralyse the isolated intestine. Condurango extract acts on the isolated intestine exactly like urazone. The intestine which has been removed immediately after death in a condition of rest from an animal which has been poisoned with papaverine behaves in a normal manner when investigated as an isolated organ. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Methane Fermentation of Ethyl Alcohol. V. L. OMELIANSKY (*Ann. Inst. Pasteur*, 1916, **30**, 56—60).—Aqueous solutions of ethyl alcohol (1%) containing, in addition, only mineral matter in amounts necessary as bacterial food have been submitted to anærobic fermentation by inoculation with fæcal matter from a rabbit which had previously received alcohol for a fortnight. The

gas collected consisted of carbon dioxide, 11·5%; methane, 87·4%; and hydrogen, 1·1%. The solid matter collected at the bottom of the liquid was used to inoculate another solution, the gas this time consisting of carbon dioxide, 12%, and methane, 88%. Fermentation in each case continued until the whole of the alcohol was decomposed, and the bacteria persisted through a series of generations for more than a year. The bacteria were examined microscopically, and presented the forms of very slender, moderately long rods, slightly bent and deprived of spores. W. G.

Influence of Pine Resin and Tannin on the Nitrogen Economy and on the Physical Properties of the Soil. ALFRED KOCH and ALICE OELSNER (*Centr. Bakt. Par.*, 1916, ii, **45**, 107—118).—In soil to which 5% of colophony and 0·025% of nitrogen as nitrate were added, the whole of the nitrate was denitrified by bacteria, which utilised the colophony as source of energy, in four weeks. The total nitrogen of the soil was only slightly diminished, so that the nitrate was utilised as source of nitrogen without liberation of free nitrogen.

In an experiment in which colophony was substituted for citric acid in a Giltay solution there was a slight reduction of nitrate to nitrite in a few days. The reduction was more vigorous in a Raulin solution, with colophony instead of sugar, owing probably to the solvent action of the potassium carbonate on the resin.

It is possible that nitrification is hindered by the presence of resin constituents dissolved by alkali salts.

Tannin is readily assimilated by mould fungi, and the increased growth of the fungi gives rise to a temporary loss of nitrogen present in the forms of ammonium salts and nitrates, which explains the low amounts of nitrates found in soils containing tannin. No oxalic acid is produced by *Aspergillus niger* from tannin.

Addition of tannin to soils results in the production of a dark colour, not due to iron. The power of retaining water is increased by addition of tannin to soils. Large additions of tannin render soils hard like stone, owing perhaps to the precipitation of colloids. N. H. J. M.

Influence of Moisture on the Nitrogen Changes in Soils. A. E. TRAAEN (*Centr. Bakt. Par.*, 1916, ii, **45**, 119—135).—Experiments on nitrification, denitrification, and fixation of nitrogen in soils. Fixation of nitrogen, like most processes in soils due to bacteria, is shown to be most active when the soil contains medium amounts of moisture. N. H. J. M.

The Ferments of Rum. E. KAYSER (*Compt. rend.*, 1916, **162**, 647—649. Compare A., 1915, i, 359, 923).—A comparison of the behaviour of bottom yeast II and yeast IV in two musts of molasses from different beetroot crops and in a must of molasses from Guadeloupe sugar cane. Each of the yeasts behaves in practically the same manner in the three media. Yeast IV always gives a notably lower proportion of higher alcohols, and a consequent

diminution of the non-alcohol coefficient. By using the two yeasts together, very wide variations in the non-alcohol coefficient can be obtained, according to the temperature, the aeration, and the method of working. The yeasts required to be gradually accustomed to the beetroot must by starting with a pure sugar-cane must, and gradually adding increasing proportions of beetroot must. W. G.

Fat in Yeast. TH. BOKORNY (*Chem. Zentr.*, 1916, i, 377—378; from *Allgem. Brau. u. Hopfen Zeit.*, 1915, **55**, 1803—1808).—Experiments were carried out with the object of explaining the fat formation in yeast. Great increase of fat can be produced by the addition of carbohydrates and nitrogen to the cultures; oxygen is necessary and the temperature should not be too low. S. B. S.

Yeast Carboxylase; its Permanence in a Dry State as Compared with the Other Enzymes of Yeast. ARMINIUS BAU (*Biochem. Zeitsch.*, 1916, **73**, 340—368).—The most resistant enzymes which are still active in dried preparations twenty years old are invertase, carboxylase, maltase, melibiase, emulsin, amygdalase, lipase, and endotryptase. The most readily alterable ferments are trehalase and oxydase. Zymase, catalase, reductase, and yeast rennin do not exist in preparations which have been kept for a long time in the dried state. S. B. S.

The Relations which Exist Between the Presence of Magnesium in the Leaves and the Function of Assimilation. G. ANDRÉ (*Compt. rend.*, 1916, **162**, 563—566).—Leaves from horse-chestnut, lilac, and chestnut trees gathered at different dates between April and October were extracted with hot ether and alcohol, and the amounts of magnesium and phosphoric acid were estimated both in the extracts and in the insoluble residues, these being referred to as organic and residual magnesium and phosphoric acid respectively. The organic magnesium attained its maximum at the beginning of May in the case of the horse-chestnut and lilac leaves and about a week earlier in the chestnut leaves. The ratio of organic to residual magnesium attained a maximum at the beginning of May in lilac leaves, at the end of May in horse-chestnut leaves, and the middle of June in chestnut leaves. The ratios for phosphoric acid agree fairly closely with those for magnesium, and it is suggested that the maximum ratio corresponds with the maximum activity of assimilation. W. G.

The Mechanism of the Exchanges Between the Roots and the Soil. Exchanges Between the Different Tissues of the Plant. P. MAZÉ (*Ann. Inst. Pasteur*, 1915, **29**, 601—632).—The first part of the paper is a more detailed account of work already published (compare A., 1914, i, 1116; 1915, i, 631). The general conclusions drawn are that the roots tend to put at the disposal of the plant a solution of definite concentration and composition

("physiological solution"). The plant develops in the minimum of time with the maximum yield when the composition of the nutritive solution is just that of this physiological solution. If the nutritive solution is more concentrated, the roots take in proportionally more water than nutrients, and the nutritive solution becomes more concentrated. The plant adapts itself to this condition, absorption is checked, and the development of the plant retarded. Where the nutritive solution is more dilute than the physiological solution the nutrients are absorbed proportionately faster than the water. When one element is missing from the nutrient solution vegetation slackens or is arrested, the plant lives on its reserves and takes up only water from the nutrient solution, the roots becoming impermeable to salts and permeable only to water.

Two young maize plants grown in the ordinary culture liquid were taken and the roots cut off 1 cm. below the junction of root and stem. One was then placed with the small length of main root in the culture liquid and the other in distilled water, and they were exposed to sunlight for seven hours, an uncut control plant growing in the culture liquid being placed alongside. At the end of the seven hours the first plant had lost its turgescence and the lower leaves were withered, the upper leaves being curled at their extremities. Similar but less marked symptoms were noticeable in the second plant. Twenty-four hours after, at the end of a second sunny day, both plants were quite withered, not having regained their normal aspect during the night. Kept in these conditions for a number of days, the plants deprived of their roots regained a certain amount of their activity, but showed all the signs of a dearth of mineral matter. W. G.

The Mechanism of the Exchanges Between the Roots and the Soil. Exchanges Between the Different Tissues of the Plant. P. Mazé (*Ann. Inst. Pasteur*, 1916, **30**, 117—140. Compare preceding abstract).—A theoretical discussion of the movements of the sap in the plant and the forces controlling them in the light of the work already published (*loc. cit.*). As a general rule, the absorption of incomplete solutions by roots or detached organs does not occur. The dissolved substances at a suitable concentration can produce plasmolysis of the protoplasmic cells, but the plasmolysis must be considered as a phenomenon of coagulation. The absorption of the sap is regulated by the chemical activity of the plant, and it is the imbibition of water aided by atmospheric pressure which causes the rise of the sap, whatever may be the height of the plant. The pressure of the sap, exudations, loss of turgescence are all indicative of variations of pressure in the interior of the plant, the variations arising from lack of equilibrium between absorption and vaporisation. The inequality of the internal pressure on the two faces of a stem, caused by light from one direction, produces phototropic orientation of this stem. The circulation of the elaborated sap is assured by the pressure of turgescence of the assimilating cells. This pressure can only

exist in the dark, and thus the circulation of the elaborated sap is a periodic phenomenon. The exchanges between the elaborated sap and the different tissues of the plant are brought about by the mechanism which governs absorption. The accumulation of soluble nutrients in the reserve cells is similarly explained, but it does not produce a mechanical pressure in the interior of the cells.

W. G.

Rapid Action of Saline Solutions on Living Plants; Reversible Displacement of a Part of the Basic Substances contained in the Plant. HENRI DEVAUX (*Compt. rend.*, 1916, **162**, 561—563).—Various aquatic plants and the stems of certain terrestrial plants were immersed first in distilled water for half an hour, then in a solution of potassium chloride or ammonium chloride (1 in 1000), and then again in distilled water. No calcium could be detected in either lots of distilled water, but could be readily detected in the chloride solutions. This decalcification of the plant is accompanied by a fixation of the base of the salt used, either ammonium or potassium, and these can in turn be removed by a subsequent immersion of the plant in a solution of calcium chloride. The action is thus reversible. The decalcifying salt may be either the chloride, nitrate, sulphate, or carbonate of potassium. sodium, ammonium, lithium, or magnesium, and the amount of calcium removed depends on the length of the immersion. There is thus a similarity between the absorbing power of the soil for saline solutions and that of living plants. The fixation occurs essentially with the basic portion. W. G.

Action of Manganese, Iron, and Copper on the Growth of Plants. HANS VAGELER (*Landw. Versuchs-Stat.*, 1916, **88**, 159—242).—Water-culture experiments with oats, lupins, and beans; pot experiments (sand and soil) with oats and lupins; and field experiments with oats. In the water cultures the amounts of manganese sulphate, iron sulphate, and copper sulphate employed were respectively 0·482, 0·556, and 0·042 gram per litre.

No stimulating effects were observed in the water-culture experiments, and addition of calcium and sodium chlorides failed to diminish the poisonous effects, which were much the greatest in the case of copper sulphate. Beans are, however, much less sensitive to copper than oats.

In the pot experiments, iron and copper slightly reduced the yield of oats, especially in sand, whilst manganese had no effect either in sand or in loam. Lupins were benefited both by iron and copper, but not by manganese.

In the field experiments, the three metals had practically no effect. N. H. J. M.

Migration of Betaine in Plants. V. STANĚK (*Zeits. Zuckerind. Böhm.*, 1916, **40**, 300—308).—The dry matter of young leaves contains more betaine than that of older leaves, and the relation of betaine to total nitrogen is also higher in the younger leaves. As ripening proceeds and the leaves die, the betaine disappears along

with the other forms of nitrogen; the relation of betaine to total nitrogen at the same time becomes lower, and it seems probable that the betaine migrates to the root at the end of the vegetative period.

Betaine is formed during the germination of seeds. During the sprouting of sugar-beet it accumulates in the leaves, and at the same time disappears from the roots. The accumulation also takes place in etiolated leaves. N. H. J. M.

A Substance which Coagulates Inulin and Accompanies it in Plant Tissues. JULES WOLFF (*Compt. rend.*, 1916, **162**, 514—516).—The author has discovered in the roots of chicory and dahlia a substance which he names *inulo-coagulase*, which coagulates inulin in the expressed juices. It is destroyed at about 60° and is much more abundant in the outer than in the central portions of the root. It is precipitated by alcohol from its aqueous solution, together with the salts which accompany it. Its action is specific in that it does not coagulate other substances, such as starch, milk, pectin. The inulin is only coagulated when expressed in the juice from the tissues of the plant, and no change is produced in the nature of the inulin by the coagulation. W. G.

Occurrence of Sucrose in Grapes of American Origin. H. C. GORE (*J. Ind. Eng. Chem.*, 1916, **8**, 333—334).—Of 66 varieties of American grapes examined during four seasons, 43 did not contain sucrose, 10 contained sucrose occasionally, whilst 13 contained it in appreciable quantity. W. P. S.

Occurrence of Relatively Large Amounts of Sucrose in a New Seedling Grape. W. B. ALWOOD and J. R. EOFF, Jun. (*J. Ind. Eng. Chem.*, 1916, **8**, 334—335).—Although sucrose has never been found in European grapes, it occurs in many varieties of American origin, including the *Vitis rotundifolia* and *V. labrusca* species. A seedling grape from Ohio, probably belonging to the *V. labrusca* species, was examined for a period of sixty days during the season of 1911; it contained a considerable proportion of sucrose. On August 23rd the quantity of sucrose was 6·66%, and increased to 10·25% by September 27th, when the grapes were fully ripe; the quantity then decreased gradually until, on October 18th, the over-ripe and falling fruit contained only 7·13%. During August and September the quantity of invert-sugar present was approximately equal to that of the sucrose and showed the same increase; a decrease did not, however, take place in the quantity of this sugar as the grapes became over-ripe.

W. P. S.

Quercetin from the Bark of Pinus pinaster. ROBERTO LEPETIT and CARLZ CARTA SATTA (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 322—325).—The yellow colouring matter obtained by treatment of the extract of the bark of the Tuscany pine with sodium hydrogen sulphite under pressure, and formerly regarded as fisetin (compare Lepetit, Atti VI. Congr. Chim. Applicata,

Rome, 1905, III., 156), is now shown, by means of its colouring properties and the constants of several of its derivatives, to consist of quercetin. T. H. P.

Lucerne. VI. Lucerne Seed Oil. C. A. Jacobson and August Holmes (*J. Amer. Chem. Soc.*, 1916, **38**, 480—485. Compare A., 1914, i, 1193).—Lucerne seed oil is a drying oil resembling safflower oil, which is conveniently isolated, to the extent of 9—10% of the seed, by percolation with light petroleum (b. p. 65—95°/645 mm.). It is chestnut-brown in colour and has the following characteristics: D_4^{24} 0·9117, n^{20} 1·4770, saponification number 172·3, iodine number 154·2, acid number 2·85, acetyl number 19·8, Reichert-Meissl number 0·40, unsaponifiable matter 4·40%, glycerol 1·97%, saponification number of the acetylated oil 192·2. It was examined by the usual methods, and found to contain practically no volatile acids, but about 92·5% of insoluble fatty acids, of which 90·4% are liquid, comprising oleic, linoleic, and linolenic acids, and 9·6% are solid, including carnaubic, daturic, and possibly behenic acids. J. C. W.

Comparison of Methods for Determining the Lime Requirement of Soils. J. W. Ames and C. J. Schollenberger (*J. Ind. Eng. Chem.*, 1916, **8**, 243—246).—The methods investigated were those proposed by Veitch, Hopkins, Hutchinson and MacLennan (A., 1914, ii, 784), and MacIntire (evaporation of the soil with calcium hydrogen carbonate and estimation of the excess of calcium carbonate), and the vacuum method (heating the soil with finely divided calcium carbonate under reduced pressure). In cases where soils had been treated with acid phosphate, bone meal, or basic slag, a higher lime requirement for the soil treated with acid phosphate was indicated by the Hopkins, MacIntire, and Hutchinson methods; the Veitch and vacuum methods gave slightly higher results for the soil treated with bone meal, whilst the Hutchinson method gave the same result for both the bone meal and basic slag plots. The variations shown by the several methods indicate their possible usefulness for comparative purposes where different soil treatments have been made. W. P. S.

Carbon and Nitrogen Changes in Soil Variously Treated: Soil Treated with Calcium Carbonate, Ammonium Sulphate, and Sodium Nitrate. R. S. Potter and R. S. Snyder (*Soil Science*, 1916, **1**, 76—94).—The soil employed was a silt loam containing 1·35% of carbon and 0·1137% of nitrogen; its lime requirement was 600 lb. per acre according to the Veitch method. The amounts of ammonia and carbon dioxide given off by the soils, both alone and with addition of ammonium sulphate and sodium nitrate respectively, without and with calcium carbonate, were estimated by passing air over the soil contained in pots under bell-jars, and then successively through standard acid and 5% potassium hydroxide.

Considerable amounts of carbon dioxide were given off during the first two days from the soil alone and from the soil with sodium nitrate; with ammonium sulphate the amount was much higher;

and with calcium carbonate very much higher, whether employed alone or in conjunction with the nitrogenous manures. The production of carbon dioxide rapidly fell, but remained highest in the pots which received calcium carbonate. As regards the origin of the carbon dioxide, it is shown that in this experiment addition of calcium carbonate diminished its production from the organic matter; in another experiment the organic matter yielded more carbon dioxide when calcium carbonate was added than without.

The loss of ammonia amounted to about 0·3 lb. per acre in twelve weeks, and was only higher (about ten times) in the pots which received both calcium carbonate and ammonium sulphate.

The losses of total nitrogen were generally less and the gains greater when calcium carbonate was added than without it.

N. H. J. M.

Activity and Availability of Insoluble Nitrogen in Fertilisers as Shown by Chemical and Vegetation Tests. F. R. PEMBER and BURT L. HARTWELL (*J. Ind. Eng. Chem.*, 1916, **8**, 246—251).—Rye and oat plants showed variations in growth during the autumn and early spring, but the amount of nitrogen removed in the tops of the plants was much the same; although the rye plants did not make as large a growth as the oat plants, the relative growth was about the same with those having like treatment. Plants having their nitrogen added in the form of garbage tankage or aluminium nitride made no larger growth than did those to which no nitrogen was added; nitrogen in water-extracted blood proved to be just as available to the oat plant as that in unwashed blood. Animal tankage proved to be as efficient as blood; castor pomace and rape meal were also found to be excellent sources of nitrogen for oat plants. Cyanamide, added to the soil in quantity equivalent to 165 lb. of nitrogen per acre, proved to be toxic to the young plants, but they were able to overcome this and make a fair growth. The nitrogen in soot had an availability of 56 compared with that in blood at 80; oxamide, blood, and sodium nitrate were found to be equally valuable as regards their nitrogen content. Fifty-six fertilisers were tested by the vegetation test and also by the alkaline and neutral permanganate methods. About the same percentage of inferior samples was detected by the two permanganate methods, but the neutral method condemned some samples which proved to have satisfactory availabilities according to the vegetation test.

W. P. S.

Increase of Nitrogen in Fermenting Manures. W. E. TOTTINGHAM (*J. Biol. Chem.*, 1916, **24**, 221—225).—The amount of nitrogen in a fermenting mixture of cow and horse manure, with and without litter in the form of barley straw, increases during the first few weeks of fermentation and then decreases to a point below the original amount present. The gain of nitrogen is greater in the straw-littered manure, and amounts, in some cases, to 4·7% of the total nitrogen in the manure. The action is ascribed to the presence of nitrogen-fixing bacteria.

H. W. B.

Organic Chemistry.

Preparation of *iso*Propenylacetylene. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 290558; from *J. Soc. Chem. Ind.*, 1916, **35**, 558).—iso*Propenylacetylene* is obtained by heating β-methylbutinenol with a dehydrating agent,

$$OH\cdot CMe_2\cdot C{:}CH \longrightarrow CH_2{:}C(CH_3)\cdot C{:}CH + H_2O.$$

The homologues and analogues of β-methylbutinenol give a similar reaction. This result was not anticipated, as γ-methylbutinenol decomposes into acetone and acetylene on heating, and compounds with triple bonds in general either decompose or polymerise under this treatment. G. F. M.

Reaction between Alcohols and Aqueous Solutions of Hydrochloric and Hydrobromic Acids. JAMES F. NORRIS, MURIEL WATT, and RUTH THOMAS (*J. Amer. Chem. Soc.*, 1916, **38**, 1071—1079).—Norris (A., 1907, i, 1035) has shown that alkyl bromides and iodides can be prepared by distilling a mixture of the alcohol with a large excess of hydrobromic or hydriodic acid of constant b. p., and that in certain cases alkyl chlorides can be obtained in a similar manner. The investigation has now been extended to allyl, *tert.*-amyl, *n*-octyl, *sec.*-octyl, $\alpha\alpha\beta\beta$-tetramethylpropyl, cetyl, *o*-, *m*-, and *p*-nitrobenzyl, α-phenylethyl, γ-phenylpropyl, and cinnamyl alcohols, and the results have led to the following conclusions.

The rate of reaction of primary alcohols with aqueous hydrobromic acid (D 1·49) decreases as the molecular weight of the alcohol increases. Tertiary alcohols react more readily than secondary alcohols, and secondary more readily than primary alcohols. The reactivity of alcohols with hydrochloric acid is facilitated by the accumulation of negative groups around the carbinol carbon atom; this is illustrated by the facts that benzyl and allyl alcohols react readily with aqueous hydrochloric acid whilst ethyl alcohol does not, and that cinnamyl alcohol gives a yield of 80% of the chloride when distilled with hydrochloric acid (D 1·1), whereas γ-phenylpropyl alcohol, $CH_2Ph\cdot CH_2\cdot CH_2\cdot OH$, does not give any chloride under these conditions. All the twenty-seven alcohols which have now been studied form bromides when heated with hydrobromic acid of constant b. p., and it is therefore suggested that the reaction may be employed as a trustworthy test for an alcoholic hydroxyl group. In all cases good yields of the bromides and iodides are obtained, and the reactions can be used with advantage for the preparation of these compounds.

The foregoing statements refer only to monohydric alcohols, but a study of polyhydric alcohols has been begun, and the results so far obtained show that, when boiled with aqueous hydrobromic acid, ethylene glycol is partly converted into ethylene dibromide, and glycerol into a bromohydrin, b. p. 145—147° (corr.)/30 mm.

E. G.

Vapour Pressure of Glyceryl Trinitrate (Nitroglycerin) at the Ordinary Temperature. D. CHIARAVIGLIO and O. M. CORBINO (*Gazzetta*, 1916, **46**, i, 368—370).—Marshall and Peace's statement (T., 1916, **109**, 299) that the authors' measurements of the vapour pressure of glyceryl trinitrate were made in the presence of phosphoric oxide is erroneous (A., 1913, i, 1299); they have ignored the authors' later work (A., 1914, i, 478), which gave for the vapour pressure at 25° the value 0·00012 mm. T. H. P.

Solubility Data for Various Salts of Lauric, Myristic, Palmitic, and Stearic Acids. C. A. JACOBSON and AUGUST HOLMES (*J. Biol. Chem.*, 1916, **25**, 29—53).—Tables are given showing the solubility of the lithium, magnesium, glucinum, barium, lead, and silver salts of the above acids in two or more of the following solvents: water, ethyl and methyl alcohols, ethyl ether, benzene, ethyl acetate, methyl acetate, amyl alcohol, amyl acetate, chloroform, and acetone, at room temperature, 25°, 35°, and 50°, whenever the boiling point of the solvent permitted.

The solubility of all the salts examined is only slight, varying between 6% and virtual insolubility. The lithium salts are about three times as soluble in acetone and methyl alcohol as the magnesium salts, whilst the latter are more soluble in ethyl alcohol than the former. The best general solvent for this class of substances is methyl alcohol. H. W. B.

Separation of Lauric and Myristic Acids from Each Other and from Mixtures of Other Fatty Acids. C. A. JACOBSON and AUGUST HOLMES (*J. Biol. Chem.*, 1916, **25**, 55—61).—The authors briefly describe a method for the separation of lauric acid when present in a mixture containing myristic, palmitic, and stearic acids, and also a method for the separation of myristic acid from a mixture containing palmitic and stearic acids. These methods are based on the differences of the solubility of their lithium and magnesium salts in water and 50% alcohol. H. W. B.

Fatty Oils in the Light of Mesomorphous Polymerisation. A. KRONSTEIN (*Ber.*, 1916, **49**, 722—732).—It has long been known that when castor oil is heated a certain amount of heptaldehyde distils over and then the residue suddenly becomes gelatinous, whereas most other fatty oils can be distilled almost to the last drop. Wood oil, however, becomes gelatinous almost as soon as it is heated. These phenomena are explained in terms of the author's idea of mesomorphous polymerisation (A., 1903, i, 80). All the fatty oils are regarded as mixtures of glycerides, which can undergo mesomorphous polymerisation, with others which do not polymerise on heating. The presence of the latter does not hinder the formation of intermediate polymerides of the former, but does influence, and may entirely prevent, the full extension of the process to the production of gelatinous substances. A mixture which does not actually coagulate will, however, thicken, owing to the formation of the intermediate products, and it may be made

into a coagulable mixture by adding sufficient of an oil which does polymerise readily, or by removing sufficient of the non-polymerising portions by vacuum distillation. The latter point has a practical application, for the "distillation number," namely, the percentage of an oil which must be removed by vacuum distillation before the residue coagulates, that is, before distillation ceases, is characteristic for different oils. The following examples are given: drying oils: wood oil, 0%; linseed oil, 16·4%; perilla oil, 18·5%; hemp oil, 20·5%; nut oil, 24%; poppy oil, 24·5%; sunflower oil, 25%; semi-drying oils: soja bean oil, 25·4%; almond oil, 33%; cotton oil, 33·6%; maize oil, 35·5%; sesame oil, 42·5%; rape oil, 35·6%; non-drying oils: castor oil, 48%; earth nut oil, 53%; olive oil, 54%. The connexion between the drying capacity and the polymerisation of the oils is discussed.

The depolymerisation of a mesomorphous polymeride is a difficult matter, and only proceeds as far as the intermediate polymerides. In the case of the oils, this can only be done by allowing the gelatinous mass to cool completely before heating it again. Then it changes into a viscous liquid, which remains liquid on cooling, or re-gelatinises if heated sufficiently, that is, the intermediate polymerides are present in it. J. C. W.

Occurrence of Azelaic Acid as a Product of the Spontaneous Oxidation of Fats. BEN H. NICOLET and LEONARD M. LIDDLE (*J. Ind. Eng. Chem.*, 1916, **8**, 416—417).—The oil obtained from a specimen of Fuller's earth which had been used to bleach cotton-seed oil and had been kept exposed to the air for eighteen months, yielded a quantity of azelaic acid amounting to 10% of the weight of the oil extracted from the earth. Only a small proportion of the azelaic acid was present in the free state, the greater part being obtained after saponification, a fact which points to the formation of glycerides of dibasic acids, or of mixed glycerides containing these acids, during oxidation. W. P. S.

Cerebronic Acid. PERCY BRIGL (*Zeitsch. physiol. Chem.*, 1915, **95**, 161—194. Compare Levene and Jacobs, A., 1912, i, 936; Levene and West, A., 1913, i, 587).—The cerebronic acid used by Levene and his co-workers melted 16° higher than Thierfelder's crystallised cerebronic acid, and appears to have been identical with neurostearic acid. On reduction with phosphorus and hydriodic acid, a hydrocarbon was obtained which was assumed to be *n*-pentacosane. The author has now synthesised both *n*-pentacosane and the corresponding hydroxy-acid, α-hydroxy-*n*-pentacosoic acid, in order to compare them with the substances obtained from natural cerebrone. Cerebronic acid melts 3° lower than the synthetic acid, and the preparation of the natural hydrocarbon has not been completed owing to the war.

The starting point for the synthesis of *n*-pentacosane was cetylmalonic acid, from which the *ethyl* ester, b. p. 238—240° (14 mm.), yellow liquid solidifying to a white, lardaceous mass, m. p. 22°, was prepared by the successive action of thionyl chloride and ethyl

alcohol. The ester is treated with *n*-octyl iodide and sodium, and the product hydrolysed and purified by means of the barium salt. *Octylcetylmalonic acid*, $C_{16}H_{33}\cdot C(C_8H_{17})(CO_2H)_2$, colourless needles from acetic acid, m. p. 68°. On heating at 150°, it loses 1 mol. CO_2, forming *octylcetylacetic* [*α-octylstearic*] *acid*,

$$C_{16}H_{33}\cdot CH(C_8H_{17})\cdot CO_2H,$$

white powder, m. p. 52°.

The removal of the second molecule of carbon dioxide by heating the *barium* salt of α-octylstearic acid with sodium methoxide yields a mixture of products, the separation and purification of which present great difficulties. The desired cleavage can be effected, however, by treating α-octylstearic acid with phosphorus and excess of bromine at 100°, dissolving the product in ether and then saturating with ammonia, whereby *α-bromo-α-octylstearamide*, $C_{26}H_{52}ONBr$, is formed (white, crystalline mass, m. p. 49—51°). On heating the latter product in alcoholic solution with sodium, and pouring into boiling water, an oil separates which solidifies on cooling and can be recrystallised from benzene. *ι-Pentacosanone*, (*octyl cetyl ketone*), $C_{16}H_{33}\cdot CO\cdot C_8H_{17}$, has m. p. 66°, forms a *semicarbazone*, $C_{26}H_{53}ON_3$, m. p. 39—41°, and on reduction of its chloride with phosphorus and hydriodic acid yields *n-pentacosane*, $C_{25}H_{52}$, glittering, white plates from alcohol, m. p. 55·5—56°. Its identity with the natural pentacosane (m. p. 54°) occurring in petroleum and in lignite has not been established.

Prior to the synthesis of α-hydroxy-*n*-pentacosoic acid, *n*-tetracosoic acid was prepared in a manner similar to that since described by Meyer, Brod, and Soyka (A., 1913, i, 1151). The characteristics of the following intermediate products differ from those given by Meyer and his collaborators: docosyl iodide, m. p. 48·5—50°; docosylmalonic acid, m. p. 126°; *ethyl docosylmalonate*, m. p. 48·5—49°. The chloride of behenic acid was also prepared, m. p. 40° (Meyer gives 73—75°), which on treatment with ethyl carbimide and subsequent hydrolysis with aqueous acetone yields the *ethylamide* of α-ketotricosoic acid, $C_{21}H_{43}\cdot CO\cdot CO\cdot NHEt$, needles from alcohol, m. p. 91—92°. When boiled with phenylhydrazine, the amide forms the *phenylhydrazone*, $C_{31}H_{55}ON_3$, m. p. 96—98°. As both the latter derivatives resisted hydrolysis, the amide was reduced by means of aluminium amalgam to the *ethylamide* of α-hydroxytricosoic acid, $C_{21}H_{43}\cdot CH(OH)\cdot CO\cdot NHEt$, m. p. 113—115°, which after acetylation was hydrolysed by a mixture of acetic and hydrochloric acids, yielding α-hydroxytricosoic acid.

The *ethylamide* of α-ketopentacosoic acid, m. p. 94—95·5°, and the *ethylamide* of α-hydroxypentacosoic acid,

$$C_{23}H_{47}\cdot CH(OH)\cdot CO\cdot NHEt,$$

m. p. 115—117°, are prepared in a similar way to that described above, and from the latter, by acetylation followed by hydrolysis, the synthetic *α-hydroxypentacosoic acid*, $C_{23}H_{47}\cdot CH(OH)\cdot CO_2H$, microcrystalline powder, m. p. 102—104°, is obtained. The relation of the natural, dextrorotatory cerebronic acid to the synthetic, inactive α-hydroxypentacosoic acid has not been definitely established.

H. W. B.

Preparation of Acetaldehyde from Acetylene. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (Eng. Pat., 1915, 5132; from *J. Soc. Chem. Ind.*, 1916, **35**, 556—557).—The velocity of the catalytic hydration of acetylene in presence of a mercury salt is greatly increased by carrying out the reaction in glacial acetic acid solution at 80—90°, water being added as required during the reaction. The acetic acid may be partly replaced by ethylidene diacetate. Thus, when acetylene is led into a well-stirred mixture of 1000 grams of glacial acetic acid, 22·5 grams of concentrated sulphuric acid, and 100 grams of mercuric oxide at 80—85°, it is absorbed at the rate of 100—200 litres per hour, and water is added at the same rate as it is used up. The products of the reaction are passed through a fractionating apparatus, a condenser cooled by a freezing mixture, an absorption vessel charged with water in which the acetaldehyde is retained, and the excess of acetylene is led back into the reaction vessel. The latter may be of iron or nickel. Mercuric salts of strong acids other than sulphuric acid may be employed as catalysts, and either the oxide or the acid may be in excess. G. F. M.

Isomerism of the α- and β-Forms of the Sugars. ERNEST ANDERSON (*J. Physical Chem.*, 1916, **20**, 269—285).—A theoretical paper in which the author, by a comparison of the configurations and rotations of the sugars, shows that in all probability the 5-atomic lactone structure of hexoses and pentoses is incorrect. He shows that α-dextrose may have a 4-atomic lactone structure, whilst β-dextrose may have a 3-atomic lactone structure. These relationships probably hold also for all pentoses and hexoses as well as for their corresponding glucosides. The author shows that from rules connecting configuration with rotation, which he formulates, it is possible to deduce the approximate rotations of sugars of known configuration and the configuration of sugars of known rotation. A list of sixteen sugars of known rotation and configuration is considered, and every member shown to be in agreement with the author's views. The structure of *d*-manno-octose as given by Fischer and Passmore (A., 1890, 1230) is considered and shown to be at variance with the rules laid down by the author. An alternative formula is suggested. J. F. S.

Causation of Staleness of Bread-crumb Considered from the Physiological-chemical Point of View. I. J. R. KATZ (*Zeitsch. physiol. Chem.*, 1915, **95**, 104—129).—The mere drying of bread-crumb exposed to the air does not produce staleness, because bread-crumb becomes stale when kept in a hermetically sealed vessel, or even in an atmosphere saturated with water vapour. The author shows that the chief cause of staleness is the change which occurs in the starch grains of the bread, which become harder and less capable of absorbing water, whilst the soluble polysaccharides contained in them are in part transformed into an insoluble condition. The bread therefore becomes less sweet to the taste, as well as harder in consistency. Similar changes do not occur in the gluten, the absorptive power for water of which

remains unchanged. The author accounts for the crumbly nature of stale bread by the assumption that a passage of water takes place from the hardening starch grains to the particles of gluten, which lessens the adherence of the particles to one another.

The velocity of the change in the absorptive power of the crumb for water can be expressed as that of a bimolecular chemical reaction. The crumbly nature develops considerably after the decline in water-absorptive power has commenced. H. W. B.

Causation of Staleness of Bread-crumb Considered from the Physiological-chemical Point of View. II. J. R. KATZ (*Zeitsch. physiol. Chem.*, 1915, **95**, 136—146).—In order to study the changes occurring in bread during the baking process, the author has prepared from the same mass of dough four loaves, baked for 12, 20½, 31, and 55 minutes respectively, and has estimated the water-absorptive power of the bread-crumb and its content of water-soluble polysaccharides in each case. Both factors are found to increase two- or three-fold or more during the baking process, and the values when graphically expressed are seen to approach asymptotically to a definite limit. Isolated grains of wheat starch when heated with water show the same behaviour.

On comparison with the previous results (compare preceding abstract), it is observed that the process of becoming stale is accompanied by changes in the starch grains which are the reverse of those found to occur during baking. In other words, the reactions which occur in the starch during baking attain an equilibrium at the baking temperature, and on the bread becoming cool these reactions naturally tend to proceed in the reverse direction, just as the brown molecules of dissociated nitrogen peroxide pass back again on cooling into the colourless associated molecules.

In confirmation of this view, it is found that bread while maintained for twenty-four hours or more at a high temperature (60°) in a closed vessel remains perfectly fresh. H. W. B.

Causation of Staleness of Bread-crumb Considered from the Physiological-chemical Point of View. III. J. R. KATZ (*Zeitsch. physiol. Chem.*, 1915, **95**, 147—151. Compare preceding abstracts).—The changes occurring in the starch grains during the process of baking bread, and the reverse changes which take place afterwards, which result in the bread becoming stale, are not peculiar to wheat starch. Similar changes are observed with rice, potato, arrowroot, lentil, barley, maize, sago, and oat starches. On heating the starch with 45% of water in a closed tube at 100° during fifteen minutes, the capacity for absorbing water and the content of soluble polysaccharides are both increased. After remaining for twenty-four hours, the starch has more or less returned to its former condition. H. W. B.

Alterations in the Microscopic Structure of Bread During the Process of Becoming Stale. E. VERSCHAFFELT and (FRL.) E. VAN TEUTEM (*Zeitsch. physiol. Chem.*, 1915, **95**, 130—135).—In new

bread the starch grains are surrounded by gluten. After nine hours air spaces or vacuoles appear between the edge of the starch grain and the surrounding gluten, and this appearance is concomitant with the development of the "crumbly" condition associated with stale bread (compare preceding abstract). For microscopic examination, thin fragments of the bread are suspended in safranine solution, which stains the gluten deep pink, whilst the starch grains remain almost colourless. H. W. B.

Reactions and Constitution of Lignone. C. F. CROSS and E. J. BEVAN (*J. Soc. Dyers*, 1916, **32**, 135—141).—Treatment with somewhat less than 0·5% of its weight of hydroxylamine converts lignocellulose into a product containing 0·18% of nitrogen which no longer gives the characteristic colour reactions. These are therefore due to associated aldehydic substances, and are not primary characteristics of the lignone complex. Nevertheless, the amount of such substances present in natural lignone is so constant as to afford a quantitative measure of the lignocellulose itself. For this purpose it is preferable to determine the gravimetric ratio of phloroglucinol in combination with the lignone rather than to rely on colour-scale tests. For a number of specimens of jute the phloroglucinol absorption was 3·1—4·2% dry fibre, whilst for wood meals, etc., it ranged from 6·8—7·8%. In these reactions the hydrochloric acid added plays an active rôle. Jute fibre after six days' digestion with 33% hydrochloric acid lost 17% in weight, and the residue gave none of the reactions of furfuraldehyde derivatives. From the products of digestion 3% and 6·95% respectively of volatile acid (calculated as acetic acid) were obtained, in the latter case after oxidation with chromic acid. Digestion with ethereal hydrogen chloride solution gave rise, on the other hand, to no volatile acid, a condensation rather than a rupture of cyclic products having been brought about. From a study of the disintegration of lignone by chromic acid in presence of varying concentrations of sulphuric acid, it is evident from the proportions of acetic, oxalic, and carbonic acids produced in the different circumstances that hydrolysis is an important factor of the resolution, and that there is a residue in lignone which may appear as a component of the fibrous "oxycellulose" complex and not undergo oxidation to end-products of low molecular weight. This is identified as 3-hydroxy-2-methyl-γ-pyrone, usually known as maltol, and it is produced from lignocellulose by heating in sealed tubes at 150° or in open tubes to just visible colour change. The paper concludes with a résumé of the relationships of heat, light, and electricity to celluloses and their derivatives. G. F. M.

The Reaction of Aliphatic Imino-derivatives with Absolute Nitric Acid. A. P. N. FRANCHIMONT and J. V. DUBSKY (*Rec. trav. chim.*, 1916, **36**, 80—109).—A more detailed account of work already published (compare A., 1912, i, 752). W. G.

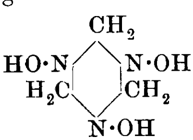
Preparation of Esters of Alkamines. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 290522; from *J. Soc. Chem. Ind.*, 1916, **35**, 558).—Alkamine esters are obtained by heating mono- or di-acidyl derivatives of urethanes with alkamines. G. F. M.

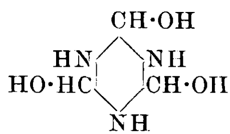
Preparation of Non-hygroscopic Salts of Choline. F. HOFFMANN-LA ROCHE & Co. (D.R.-P., 290523; from *J. Soc. Chem. Ind.*, 1916, **35**, 558).—Soluble non-hygroscopic salts of choline are prepared either by neutralising the free base with dihalogeno-hydroxybenzoic acids or by double decomposition between choline salts and salts of the above acids. G. F. M.

Preparation of Salts of an Organic Derivative of Sulphurous Acid. J. D. RIEDEL (D.R.-P. 290426; from *J. Soc. Chem. Ind.*, 1916, **35**, 557).—Salts of the hitherto unknown amino-carbonylsulphurous acid are formed by the action of alkali *iso*cyanates, such as potassium *iso*cyanate, on alkali hydrogen sulphites. Like the alkali salts of aminomethanedisulphonic acid, the new compounds react with metallic oxides, forming non-ionised salts, which are of value as starting materials for the preparation of therapeutically active substances. G. F. M.

Tautomerism. XIX. Tautomerism of the Amides. H. A. LUBS and S. F. ACREE (*J. Physical Chem.*, 1916, **20**, 323—325. Compare A., 1915, i, 90).—A preliminary paper dealing with the possible tautomerism of amides, and giving methods of preparation of glycollonitrile, glycollimido-ester hydrochloride, and glycollimidohydrin. J. F. S.

The Constitution of the Hydrochlorides Obtained from Formaldoxime and the Strength of the Bases from which they are Derived. C. H. SLUITER (*Rec. trav. chim.*, 1916, **36**, 1—23).—For the most part a more detailed account of work already published (compare this vol., i, 250). To the bases corresponding with the hydrochloride first formed and freshly crystallised, and with the hydrochloride finally obtained by drying this salt in a vacuum, that is, the hydrochloride obtained by Dunstan and Bossi (T., 1898, **73**, 353), respectively, the formulæ I and II are assigned:


(I.)


(II.)

The hydrochlorides are $(CH_2{:}N{\cdot}OH)_3,3HCl$ and $(CH_2{:}N{\cdot}OH)_3,HCl$ respectively, the molecular transposition taking place under the influence of free hydrochloric acid. W. G.

Methylarsine Dichloride. ENRIQUE V. ZAPPI (*Anal. Soc. Quim. Argentina*, 1915, **3**, 447—450).—Methylarsine dichloride,

$CH_3\cdot AsCl_2$,

can be prepared by the action of hydrochloric acid on cacodylic acid, $(CH_3)_2AsO\cdot OH + 3HCl = CH_3\cdot AsCl_2 + CH_3Cl + 2H_2O$. It has b. p. 132° and D 1·809. A. J. W.

A Space Formula for Benzene. II. JOHN NORMAN COLLIE. (T., 1916, **109**, 561—568; compare T., 1897, **71**, 1013).—An extension of the author's dynamic formula for benzene, in which it is shown how such molecules could be packed together to occupy the space lattice of the benzene crystal. J. C. W.

***o*-Chlorobenzyl Bromide and its Products of Hydrolysis.** ALFRED GODFREY GORDON LEONARD (T., 1916, **109**, 570—571).—o-*Chlorobenzyl bromide*, $C_6H_4Cl\cdot CH_2Br$, was prepared by brominating *o*-chlorotoluene, as a colourless liquid, b. p. 120°/10 mm., which has a pungent odour and gives a vapour which powerfully irritates the eyes. When boiled with aqueous alcoholic potassium hydroxide under reflux, the liquid gradually lost its irritating effect, and then distillation with steam of the product yielded, first, *o*-chlorobenzyl ethyl ether, b. p. 216°/761 mm., 103°/8 mm., followed by *o*-chlorobenzyl alcohol, m. p. 70—71°, whilst *di*-o-*chlorobenzyl ether*, $C_{14}H_{12}OCl_2$, separated on cooling the residue in the flask, in hexagonal prisms, m. p. 48—49°. J. C. W.

Exchange of Halogen in Aromatic Compounds for the Amino-group under the Influence of Finely Divided Nickel. J. P. WIBAUT (*Chem. Weekblad*, 1916, **13**, 459—463).—In presence of finely divided nickel at about 300°, ammonia reacts with chlorobenzene, bromobenzene, and *o*-chlorotoluene, producing a small yield of the corresponding amino-compound. A. J. W.

Chemical Processes Involved in the Technical Reduction of Aromatic Nitro-compounds to Amino-compounds. P. N. RAIKOW (*Zeitsch. angew. Chem.*, 1916, **29**, i, 196—199).—None of the theories advanced at various times to explain the mechanism of the reduction of aromatic nitro-compounds to amines by means of iron and only one-fortieth of the theoretical quantity of hydrochloric acid is in accordance with all the facts except that of Muspratt, which was declared by Wohl to be erroneous (A., 1894, i, 409, 450), but which has now been experimentally proved in all its stages. The amino-compound, for example, aniline, plays an active part in the process in that it converts the ferrous chloride into ferrous hydroxide, and the aniline hydrochloride thus formed then reacts with the free iron, with the formation of hydrogen and ferrous chloride, thereby completing the cycle, $2C_6H_5\cdot NH_2 + FeCl_2 + 2H_2O = 2C_6H_5\cdot NH_2,HCl + Fe(OH)_2$ and $2C_6H_5\cdot NH_2,HCl + Fe = 2C_6H_5\cdot NH_2 + FeCl_2 + 2H$. G. F. M.

Halogenation. X. Chloric Acid as a Reagent in Organic Chemistry. RASIK LAL DATTA and JOGENDRA KUMAR CHOUDHURY (*J. Amer. Chem. Soc.*, 1916, **38**, 1079—1086).—An account is given of the preparation of a number of organic chlorates, either by the

direct action of chloric acid on the base or by double decomposition of the hydrochloride of the base and silver chlorate. Chlorates of aliphatic bases can be readily obtained by either method, but more difficulty is experienced with the aromatic bases, owing to the ease with which they undergo oxidation. The chlorates are generally unstable in the dry state, and are sometimes explosive. The following compounds are described:

o-*Toluidine chlorate*, white plates, exploding at 88°; p-*toluidine chlorate*, long, white crystals, exploding at 125°; p-*phenylenediamine chlorate*, very unstable crystals; *benzylamine chlorate*, m. p. 110·5°, crystalline plates; *benzylmethylamine chlorate*, m. p. 59—60°; *benzylethylamine chlorate*, m. p. 81·5°; *piperazine chlorate*, white, lustrous plates, decomposing at 98—100°; *ethylenediamine chlorate*, lustrous, white, flat crystals, decomposing at 150°; *guanidine chlorate*, white crystals, decomposing at 148°; *menthylamine chlorate*, m. p. 168°, white needles; *pyridine chlorate*, m. p. 147° (decomp.); *quinoline chlorate*, m. p. 66—67°, pale yellow crystals; *tetraethylammonium chlorate*, white crystals, exploding at 230°; *tetraethylammonium chlorate*, m. p. 223° (decomp.); *tetrapropylammonium chlorate*, m. p. 217°; *phenylbenzyldimethylammonium chlorate*, white crystals, decomposing at 137°; *phenylbenzyldiethylammonium chlorate*, m. p. 77°; *trimethylsulphine chlorate*, exploding at 170°.

When aniline is treated with excess of chloric acid, a mixture of chloroquinones is produced, but if the aniline is in excess aniline-black is formed. If excess of chloric acid is added to *o*- or *p*-toluidine, a dark-coloured, viscous liquid is produced, whilst when the base is in excess a black dye is obtained.

When iodo-derivatives of the aromatic hydrocarbons are subjected to the prolonged action of chloric acid, iodoxy-derivatives are produced. The following compounds were prepared in this way: iodoxybenzene, *o*- and *p*-iodoxytoluene, *p*-iodoxy-*m*-xylene, iodoxymesitylene (decomposing at 194°), and p-*iodoxy*-o-*xylene*, $C_6H_3Me_2{\cdot}IO_2$, which forms yellow crystals and explodes at 192—193°. E. G.

Syntheses in the Fatty-aromatic Series. XII. Derivatives of *m*-Phenylenediamine and *m*-Nitroaniline with Regard to their Taste and Hæmolytic Action. J. VON BRAUN and MARGARETE RAWICZ (*Ber.*, 1916, **49**, 799—809).—4-Nitro-*o*-toluidine is known to be a very sweet substance, but 4:4′-dinitro-2:2′-diamino-αζ-diphenylhexane (A., 1913, i, 772) is tasteless; tolylene-2:4-diamine has a pronounced hæmolytic action, but 2:4:2′:4′-tetra-amino-αζ-diphenylhexane is inactive. The question naturally arose whether the loss of physiological action in these compounds is due to the lengthening of the aliphatic chain from methyl to hexyl or to the double appearance in the molecules of the nuclear complexes. It is shown that the latter factor is the cause, for 2:4-derivatives of benzene with a propyl group in position 1 are similar to the toluene derivatives, whilst disubstituted ethanes are as inactive as the hexane derivatives. As an extension, the effect

of substituents in the aliphatic side-chain of the propyl derivatives on the physiological activity has also received attention.

4 : 4′-*Dinitro*-2 : 2′-*diaminodibenzyl* was prepared by nitrating 2 : 2′-diaminodibenzyl in concentrated sulphuric acid. It forms orange crystals, m. p. 254°, and yields 2 : 4 : 2′ : 4′-*tetra-aminodibenzyl*, glistening, brown leaflets, m. p. 150°, on reduction. This gives all the reactions of a *m*-diamine, and may also be obtained by reducing 2 : 4 : 2′ : 4′-*tetranitrodibenzyl*, pale yellow crystals, m. p. 168—169°, which is prepared by treating dibenzyl with fuming nitric acid.

For the preparation of 4-nitro-2-aminopropylbenzene, *o*-propylaniline was necessary. This was obtained by converting tetrahydroquinoline into *o*-γ-chloropropylbenzanilide (A., 1904, i, 918), transforming this into the iodo-compound, reducing the product by means of zinc dust and a mixture of acetic and hydrochloric acids, and finally hydrolysing the *o*-propylbenzanilide. *o*-Propylaniline was thus obtained more readily than by Piccinini and Camozzi's method (A., 1899, i, 74). It was converted into the *phenylthiocarbamide*, $C_6H_4Pr^{\alpha}\cdot NH\cdot CS\cdot NHPh$, needles which soon become pink in the air, m. p. 120°, and the *di-o-propylphenylthiocarbamide*, m. p. 129°. 4-*Nitro*-2-*aminopropylbenzene*, $NO_2\cdot C_6H_3Pr^{\alpha}\cdot NH_2$, was obtained by nitrating the base, in orange-red needles, m. p. 72°, which, when diazotised, gave a brick-red *dye*, m. p. 180°, with dimethylaniline and a dark red *dye*, m. p. 156°, with β-naphthol. On reduction, it yielded 2 : 4-*diaminopropylbenzene* as a snow-white mass, m. p. 24—25°, b. p. 176°/14 mm., which formed a *hydrochloride*, m. p. 190°, a reddish-yellow *picrate*, m. p. 179°, and a *dibenzoyl* derivative, m. p. 233°.

5-Nitro-2-γ-dimethylaminopropylaniline,

$$NO_2\cdot C_6H_3(NH_2)\cdot CH_2\cdot CH_2\cdot CH_2\cdot NMe_2$$

(A., 1913, i, 1381), is very bitter, which is rather remarkable, for the compound, $NO_2\cdot C_6H_3Pr^{\alpha}\cdot NH_2$, is sweet, and the other nearly related substance, $NO_2\cdot C_6H_3(NH_2)\cdot NMe_2$, is tasteless. 2 : 4-*Diamino*-γ-*dimethylaminopropylbenzene*, $C_6H_3(NH_2)_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NMe_2$, was obtained by reducing the above nitro-aniline, as a viscous oil, b. p. 214—216°/16 mm.

Ethyl γ-4-*nitro*-2-*aminophenylbutyrate* was obtained by nitrating the ethyl aminophenylbutyrate (A., 1907, i, 524) in orange-red needles, m. p. 64°; it yielded a *hydrochloride*, m. p. 112°, an *acetyl* compound, m. p. 62°, and a *phenylthiocarbamide*, m. p. 118°. The ester was hydrolysed by cautiously evaporating it with hydrochloric acid, when γ-4-*nitro*-2-*aminophenylbutyric acid*, $NO_2\cdot C_6H_3(NH_2)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, was obtained in golden-yellow needles, m. p. 131° (*hydrochloride*, leaflets, m. p. 168°). Strange to say, the acid is tasteless, whereas the unsubstituted propylnitroaniline and 4-nitro-2-aminobenzoic acid are sweet. An attempt was made to prepare the acid by nitrating the hydrochloride of the corresponding anilinobutyric acid (*ibid.*), but the chief product was the nitrated *lactam*,

$$NO_2\cdot C_6H_3{<}{\substack{CH_2\cdot CH_2\\ NH—CO}}{>}CH_2,$$

which formed reddish-brown needles, m. p. 225°. The lability of the acid was also demonstrated by diazotising the ester in solution in 8% sulphuric acid, whereby a *nitroindazylpropionic acid*,

$$NO_2\cdot C_6H_3{<}\begin{matrix} C\cdot CH_2\cdot CH_2\cdot CO_2H \\ N\cdot NH \end{matrix},$$

was obtained as a golden-yellow, crystalline powder, m. p. 243°. The ester was also reduced by means of stannous chloride to γ-2:4-*diaminophenylbutyric acid*, $C_6H_3(NH_2)_2\cdot C_3H_6\cdot CO_2H$, a pale yellow powder, m. p. 159°, which formed a *dichloride*, m. p. 208°, and a *dibenzoyl* derivative, m. p. 154°, but, unlike the mono-amino-acid, showed no tendency to change into a lactam.

J. C. W.

The Nitration of some Derivatives of Phenol. (MLLE.) J. M. A. HOEFLAKE (*Rec. trav. chim.*, 1916, **36**, 24—63).—A quantitative study of the nitration of mono-, di-, and tri-phenyl phosphates, neutral phenyl carbonate, and methyl phenyl carbonate. For certain phenyl esters of the fatty series only qualitative results were obtained. The results obtained for the three phenyl phosphates differed considerably from those of Rapp (compare A., 1884, 1337), who only found the *p*-nitrophenyl ester in each case.

Diphenyl phosphate, Ph_2HPO_4, was obtained as slender needles, m. p. 70° (Rapp gave 56°), and yielded a *hydrate*, $Ph_2HPO_4,2H_2O$, colourless plates, m. p. 51°.

The method of analysis of the nitrated esters consisted in saponifying the mixed esters and separating the mixed nitrophenols by steam distillation. The amount of *o*-nitrophenol present in the distillate was determined by Crismer's method, by observing the variation produced by the nitrophenol on the critical temperature of solution of the system water–phenol. Using pure *o*-nitrophenol, a curve was constructed which showed the relationship between the maximum temperatures of solution and the concentration of the *o*-nitrophenol with respect to 100 grams of phenol. A similar preliminary trial was made with pure *p*-nitrophenol, and it was found that the very slight variations produced by this compound came within the limits of experimental error.

The final mode of procedure adopted consisted in slowly adding the ester to the nitric acid (D 1·51 for triphenyl phosphate, D 1·49—1·50 for the other esters) at −5° to −10°, pouring the product into water, adding strong potassium hydroxide solution in excess, and heating on a water-bath. The amount of alkali used and the time of heating varied with the ester. The liquid was then acidified with sulphuric acid and extracted with benzene. The benzene was distilled off, the last portion being removed in the presence of alkali. The residue was acidified again with sulphuric acid, keeping the volume below 200 c.c. and steam-distilled. The distillate was collected and weighed, the calculated amount of phenol added, and the maximum critical temperature of solution determined, from which the percentage of *o*-nitrophenyl ester in the mixture with its para-isomeride was calculated.

The amounts of *o*-nitrophenyl ester obtained were as follows: Triphenyl phosphate, 5·6%; diphenyl phosphate, 16·0%; phenyl phosphate, 16·3%; phenyl carbonate, 10·7%; phenyl methyl carbonate, 14·9%.

A qualitative examination showed the absence of *o*-nitrophenol in the solution after the saponification of the nitrated product of phenyl stearate, the presence of traces in the case of phenyl valerate, and the presence of a considerable quantity in the case of phenyl acetate. In the case of phenyl acetate three rough estimations gave the values 24·2%, 25·9%, and 19·7% as the amount of *o*-nitrophenyl acetate formed. It is necessary, however, to make considerable corrections for the amount of 2:4-dinitrophenol obtained.

Di-*p*-nitrophenyl phosphate had m. p. 175° (Rapp, *loc. cit.*, gave 133·5°) and gave a *monohydrate.*

p-Nitrophenyl phosphate had m. p. 153° (Rapp gave 112°). The author considers that the compounds isolated by Rapp were really ethyl di-*p*-nitrophenyl phosphate and diethyl *p*-nitrophenyl phosphate respectively.

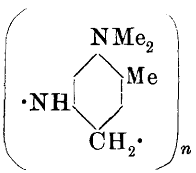
p-*Nitrophenyl carbonate*, $(NO_2 \cdot C_6H_4)_2CO_3$, had m. p. 140°. *p*-Nitrophenyl methyl carbonate had m. p. 114°. W. G.

Esters of Phenols. Jos. A. Einhorn (*Chem. Zentr.*, 1916, i, 208—209; from *Bul. Şoc. Ştiinte Bucureşti*, 1915, **17**, 110—119).—The following esters were obtained by the action of *iso*valeryl chloride and cinnamoyl chloride on the corresponding phenols: *Eugenyl* iso*valerate*, $C_{15}H_{20}O_3$, a colourless oil which becomes coloured on keeping, b. p. 219—224°/757 mm.; iso*eugenyl* iso*valerate*, $C_{15}H_{20}O_3$, a colourless, pleasant-smelling oil, b. p. 220—226°/758 mm.; 1:3:4-*xylenyl* iso*valerate*, $C_{13}H_{18}O_2$, a colourless oil, b. p. 202—203°/640 mm.; *resorcyl dicinnamate*, $C_{24}H_{18}O_4$, white, microscopic leaflets, m. p. 119·5—120°; *eugenyl cinnamate*, $C_{19}H_{18}O_3$, clusters of dark yellow, microscopic, monoclinic prisms, m. p. 90°; 1:3:4-*xylenyl cinnamate*, $C_{17}H_{16}O_2$, small, colourless, rhombic crystals, m. p. 74·5°; *pyrogallol cinnamate*, m. p 136—137°; *quinyl cinnamate*, $C_6H_4(O \cdot CO \cdot CH{:}CHPh)_2$, feathery crystals, m. p. 188·5—189·5°. G. F. M.

***tert.*-Aminobenzyl Alcohols and their Derivatives. IV.** J. von Braun (*Ber.*, 1916, **49**, 691—701. Compare A., 1912, i, 968; 1913, i, 1327, 1330).—The present investigation deals with the following questions: (1) why *tert.*-aminobenzyl alcohols do not lend themselves to condensations with aromatic bases in aqueous acidic solutions; (2) their oxidation to dialkylaminobenzoic acids by means of formaldehyde; (3) the transformation of the unsymmetrical diphenylmethane bases derived from *tert.*-aminobenzyl alcohols into unsymmetrical benzhydrols.

I. In an earlier paper it was suggested that the reason why *tert.*-aminobenzyl alcohols, unlike the primary and secondary aminobenzyl alcohols, cannot undergo condensations with aromatic amines in the presence of water, is to be found in the fact that they

cannot give anhydro-complexes. It was shown that 4-amino-6-dimethylamino-3-methylbenzyl alcohol does give a mixture of anhydro-compounds, because of the free amino-group, and therefore condenses with amines. This is supported by the behaviour of a reduction product of 6-nitro-4-dimethylamino-3-methylbenzyl alcohol. If this substance is reduced by means of stannous chloride it gives a base containing combined tin, but with zinc dust and alcoholic hydrogen chloride it yields *N*-dimethyldiamino-*m*-xylene, the product of complete reduction, which can be removed by distillation at 140—170°/11 mm., together with the *anhydro*-compound (annexed formula), which is chiefly bimolecular in dilute solutions and has m. p. 105—110°. It forms a hydrochloride, a picrate, m. p. 200°, a *nitroso*-compound, $C_{10}H_{13}ON_3$, m. p. 172°, condenses with dimethylaniline to form 2′-*amino*-4 : 4′-*tetramethyldiaminophenyl*-m-*tolyl methane*, $NMe_2\cdot C_6H_2Me(NH_2)\cdot CH_2\cdot C_6H_4\cdot NMe_2$, m. p. 145—146°, and combines with aniline to give an oil, the *dibenzoyl* derivative of which, $C_{30}H_{29}O_2N_3$, has m. p. 170°.



4-Nitro-6-dimethylamino-3-methylbenzyl alcohol, unlike the above nitro-compound, is easily converted by heating with concentrated hydrochloric acid at 120° into the *chloride*,

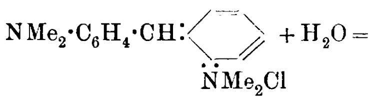
$$NMe_2\cdot C_6H_2Me(NO_2)\cdot CH_2Cl,$$

m. p. 73° (hydrochloride, m. p. 172°). This was desired for synthetical applications, but the chlorine is too readily hydroxylated. The chloride reacts with bases; for example, with pyridine it forms a *compound*, $C_{15}H_{17}O_2N_3$, m. p. 167°.

II. In the earlier papers it was briefly mentioned that if dimethyl-*p*-toluidines are heated for a long time with excess of formaldehyde, the oxidation proceeds beyond the stage of the *tert.*-aminobenzyl alcohol to the benzoic acid. New data respecting the hydrochlorides of some of these acids are now given, but the chief point to be dealt with was the proof that the oxidation of the primary alcohol group is due to the formaldehyde, and not to atmospheric oxygen. If, for example, a hydrochloric acid solution of a *tert.*-aminobenzyl alcohol is heated in an atmosphere of carbon dioxide in a sealed tube for eight days at 100° with an excess of formaldehyde, the yield of the aminobenzoic acid is more than 80%.

III. In the last paper the protection of the methylene bridge in diphenylmethanes against oxidation was examined in the case of compounds with two methyl groups or two chlorine atoms in close proximity to the bridge. The influence of the dimethylamino-group is now described. 2-*Chloro*-4 : 6′-*tetramethyldiaminophenyl*-m-*tolylmethane*, $NMe_2\cdot C_6H_3Cl\cdot CH_2\cdot C_6H_3Me\cdot NMe_2$, b. p. 228—230°/10 mm., obtained by condensing 6-dimethylamino-3-methylbenzyl alcohol with *m*-chlorodimethylaniline in the presence of zinc chloride at 140°, is not affected by lead peroxide, for the methylene group is protected by a chlorine atom and a dimethylamino-group. Similarly, 2 : 2′-tetramethyldiaminodi-*m*-tolylmethane is not oxidised. 2 : 4′-Tetramethyldiaminophenyl-*m*-tolylmethane, $NMe_2\cdot C_6H_3Me\cdot CH_2\cdot C_6H_4\cdot NMe_2(p)$, however, has only one protect-

ing group, and is oxidised by lead peroxide and acetic acid to the *hydrol*, which forms colourless crystals, m. p. 85°, and gives the characteristic colour reactions of Michler's hydrols. Unlike the paraquinonoid hydrols, however, it soon changes in solution into what is regarded as 2-*methylamino*-m-*tolyl*-4′-*dimethylaminophenylmethane*, II, m. p. 89°. The hydrol (I) is therefore assumed to be ortho-quinonoid and to change according to the scheme:

I. 

$$NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_3Me\cdot NHMe + HCl + CH_2O.$$

In the case of 5-chloro-2 : 4′-tetramethyldiaminodiphenylmethane lead peroxide also produces a hydrol, but this is very difficult to isolate. It readily changes into 5-*chloro*-2-*methylamino*-4′-*dimethylaminodiphenylmethane*, $NMe_2\cdot C_6H_4\cdot CH_2\cdot C_6H_3Cl\cdot NHMe$, m. p. 150°. J. C. W.

The Fulvene Series. CH. COURTOT (*Ann. Chim.*, 1915, [ix], **4**, 58—136, 157—224; 1916, **5**, 52—108, 194—224).—For the most part a more detailed account of work already published (compare A., 1911, i, 193, 250, 538; 1914, i, 945; 1915, i, 392, 400). Certain additional compounds have been prepared and characterised. For the preparation of a magnesium haloid derivative of *cyclo*pentadiene it is preferable to use magnesium ethyl bromide instead of magnesium methyl iodide (compare A., 1914, i, 945).

Acetaldehyde reacts with the bromo-magnesium derivative of indene to give *methylbenzofulvanol*, b. p. 133—134°/12 mm., 145—146°/19 mm., m. p. 59°, which when warmed with formic acid yields a *formate*, b. p. 142—143°/19 mm. Propaldehyde under similar conditions gives *ethylbenzofulvanol*, b. p. 147—148°/ 15 mm., 152—153°/19 mm.

Magnesium indenyl bromide, on the addition of ethereal solutions of aromatic aldehydes, gives the corresponding benzofulvanols. Thus with benzaldehyde it yields *phenylbenzofulvanol*,

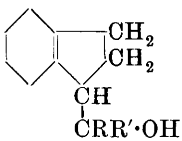
$$\begin{array}{l} CH\cdot C_6H_4 \\ \| \qquad | \\ CH\cdot CH\cdot CHPh\cdot OH' \end{array}$$

b. p. 199—200°/10 mm., which decomposes slightly during distillation. Anisaldehyde yields p-*methoxyphenylbenzofulvanol*, small prisms, m. p. 124°, which is dehydrated in boiling methyl alcohol solution by concentrated hydrochloric acid. Piperonaldehyde yields *piperonylbenzofulvanol*, m. p. 88—89°, giving a *chloride*, m. p. 114—115°. Salicylaldehyde yields o-*hydroxyphenylbenzofulvanol*, m. p. 128°. Neither the corresponding *p*-hydroxy-compound nor the fulvanol from *p*-dimethylaminobenzaldehyde could be isolated, the carbinols in each case undergoing dehydration as formed.

Ketones condense in a similar manner with the magnesium derivative of indene to give the corresponding benzofulvanols (com-

pare A., 1911, i, 193). The following were prepared: *diethylbenzofulvanol*, b. p. 154—156°/14 mm.; *phenylmethylbenzofulvanol*, b. p. 187—189°/8 mm., giving a *chloride*, slender needles, m. p. 104—105°; *phenylethylbenzofulvanol*, prisms, m. p. 64—65°. The methyl ether of *tert.*-1-indenylfluorenol [diphenylenebenzofulvanol] (A., 1911, i, 538) gives a *dibromide*, colourless, slender needles, m. p. 149°.

A number of benzofulvanols were hydrogenated in ethereal solution in the presence of platinum-black, and the resulting dihydrobenzofulvanols (formula I) were dehydrated by different methods, giving the corresponding dihydrofulvenes (formula II). The following compounds are described: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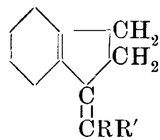
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Dihydrobenzofulvanol, a colourless liquid, b. p. 134°/13 mm., dehydrated over alumina gave *dihydrobenzofulvene*, b. p. 91—93°/17 mm.

Methyldihydrobenzofulvanol, b. p. 134°/14 mm., m. p. 45—46°, gave *methyldihydrobenzofulvene*, b. p. 103—105°/17 mm.

Ethyldihydrobenzofulvanol, needles, m. p. 65—66°; *ethyldihydrobenzofulvene*, a colourless, mobile liquid, b. p. 113—115°/17 mm.

Dimethyldihydrobenzofulvanol, b. p. 133—135°/13 mm., 145—147°/21 mm.; *dimethyldihydrobenzofulvene*, a colourless viscous liquid, b. p. 133—135°/17 mm.

Diethyldihydrobenzofulvanol dehydrated too readily on distillation to be isolated, but in this way yielded *diethyldihydrobenzofulvene*, b. p. 136—138°/15 mm.

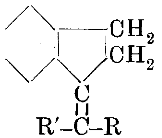
Phenyldihydrobenzofulvanol, b. p. 193—195°/13 mm., crystallises in colourless plates or agglomerates of fine needles, m. p. 65°.

p-*Methoxyphenyldihydrobenzofulvanol*, long, silky needles, m. p. 84°, is readily dehydrated in boiling alcoholic solution by concentrated hydrochloric acid, giving p-*methoxyphenyldihydrobenzofulvene*, m. p. 99—100°.

Diphenyldihydrobenzofulvanol crystallises in colourless, voluminous prisms, m. p. 90°. Dehydrated by the preceding method, it yields in four or five minutes *diphenyldihydrobenzofulvene*, m. p. 92°, but if the heating with the hydrochloric acid is continued for one hour the product is diphenyl*iso*benzofulvane [3-benzhydrylindene], m. p. 115—116° (compare A., 1915, i, 392), the double linking migrating into the nucleus (compare Wallach, A., 1908, i, 813).

The hydrogenation of the benzofulvanols by the above method is easier where the substituent is an alkyl group than where it is an aryl group.

That the dihydrobenzofulvenes have the constitution (annexed



formula) is readily shown by converting them into their ozonides in chloroform solution, the ozonide on decomposition with water giving α-indanone and the corresponding aldehyde or ketone, or an oxidation product of them. Thus dimethyldihydrobenzofulvene gave α-indanone and acetone, *p*-methoxyphenyldihydrobenzofulvene gave α-indanone and anisic acid, and diphenyldihydrobenzofulvene gave α-indanone and benzophenone.

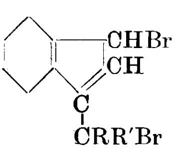
Substituted benzofulvenes are only hydrogenated by aluminium amalgam when the substituent is an aryl group, their behaviour thus resembling that of the fulvenes (compare Thiele, A., 1906, i, 569), the products obtained having the constitution

$$\begin{array}{l} CH_2\text{--}CH \\ | \qquad\ \ \| \\ C_6H_4\cdot C\cdot CHRR' \end{array}.$$

These compounds will condense with aldehydes in alcoholic solution in the presence of potassium hydroxide. Thus 3-benzylindene (compare A., 1915, i, 392) gives with benzaldehyde *benzylbenzylideneindene*, yellow needles, m. p. 137—138°. 3-Benzhydrylindene (*loc. cit.*) yields *phenyl-3-benzhydrylbenzofulvene*, golden-yellow needles, m. p. 130°.

The benzofulvenes when acted on by hydrogen in the presence of platinum-black add on four atoms of hydrogen, giving substituted methanes or, by the author's nomenclature, dihydrobenzofulvanes. The following are described: *dimethylindanylmethane*, a colourless, mobile, highly refractive liquid, b. p. 98—100°/17 mm.; p-*methoxyphenylindanylmethane*, colourless needles, m. p. 46—47°, b. p. 198—200°/10 mm.; *diphenylindanylmethane*, m. p. 85—86°.

The action of bromine on a number of these compounds was next studied. The benzofulvanols easily absorb two atoms of bromine, but, with one exception, attempts to isolate the bromo-derivatives were not successful. Diphenylbenzofulvanol gives a *dibromide*, colourless prisms, m. p. 119°. The second crop of crystals in this preparation does not consist of this dibromide, but of *dibromodiphenylbenzofulvene*, m. p. 142°, formed from it by spontaneous dehydration. The action of bromine on the dibenzofulvenes presents no special feature, except in the case of diphenyldibenzofulvene, which does not fix bromine, probably owing to steric hindrance of the two phenyl groups. The action of bromine on the fulvenes has already been studied by Thiele (A., 1900, i, 298). The two benzofulvenes studied only fixed two atoms of bromine in each case, giving compounds of the type (annexed formula). p-*Methoxyphenylbenzofulvene dibromide* crystallises in small, yellow prisms, m. p. 128—130° (decomp.), and *diphenylbenzofulvene dibromide* in pale yellow prisms, m. p. 96° (decomp.). The two dihydrobenzofulvenes examined each united with two atoms of bromine, only one of the dibromides being isolated, how-



ever, namely, *diphenyldihydrobenzofulvene dibromide*, colourless crystals, m. p. 115—117°.

In view of these new results, the author considers that Thiele's statement that in indene the double linking does not occupy a fixed position, but oscillates in the pentagonal ring, is not sound, and that most of his results are explicable on the basis of isomerisation produced by alkalis, the double linking being displaced by this reagent.

A number of substituted dibenzofulvanols have been prepared from the magnesium derivative of fluorene by the usual method with aldehydes and ketones. *Methyldibenzofulvanol*,

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH\cdot CHMe\cdot OH,$$

colourless crystals, m. p. 102—103°; *o-hydroxyphenyldibenzofulvanol*, colourless needles, m. p. 147°; *dimethyldibenzofulvanol*, prisms, m. p. 103°, giving a *chloride*, m. p. 92—93°; diphenyldibenzofulvanol (compare A., 1911, i, 538) has m. p. 216—217°.

The paper is then continued with a long historical summary of the chemistry of coloured hydrocarbons with a view to the establishment of some relationship between the colour and constitution of the fulvenes (see later).

A number of benzofulvenes have been prepared by dehydration of the corresponding fulvanols by distillation over alumina (compare A., 1915, i, 400). *Methylbenzofulvene* is a golden-yellow, mobile liquid, b. p. 119—121°/17 mm. *Ethylbenzofulvene* is a golden-yellow liquid, b. p. 140—141°/20 mm., and is much less liable to polymerisation than its lower homologues. *Piperonylbenzofulvene* was obtained from the corresponding chloride by the action of pyridine. It is an orange-yellow, crystalline compound, m. p. 113—114°. All attempts to dehydrate *o*-hydroxyphenylbenzofulvanol were unsuccessful. *p-Hydroxyphenylbenzofulvene* was obtained directly by the condensation of *p*-hydroxybenzaldehyde with the magnesium derivative of indene without the intermediate formation of the alcohol. It crystallises in plates from alcohol, and in greenish-yellow needles, m. p. 138—139°, from acetic acid. *p-Dimethylaminophenylbenzofulvene*, orange-yellow crystals, m. p. 163°, was similarly prepared by direct condensation.

Dimethylbenzofulvene, a golden-yellow oil, b. p. 129—130°/8 mm., was obtained by dehydrating the corresponding fulvanol with hydrobromic acid. On oxidation with potassium permanganate it yielded acetone and phthalic acid. *Diethylbenzofulvene*, a clear, yellow liquid, b. p. 140—142°/15 mm., is best prepared by heating its fulvanol with glacial formic acid on a water-bath for fifteen minutes. *Phenylmethylbenzofulvene*, orange-yellow crystals, m. p. 70°, is obtained by the dehydration of its fulvanol with pyridine. If the alcohol is dehydrated with hydrochloric acid by Norris's method (compare A., 1907, i, 1034), a colourless *compound*, m. p. 80°, isomeric with the above fulvene is obtained. By the condensation of Michler's ketone with the

magnesium derivative of indene, *tetramethyldi*-p-*aminodiphenylbenzofulvene*, a brick-red product, m. p. 185°, was obtained.

Dibenzofulvene could not be obtained, but certain substituted dibenzofulvenes have been prepared in addition to those already known. By the action of pyridine on the chloride of dimethyldibenzofulvanol, *dimethyldibenzofulvene*, colourless needles, m. p. 89°, was obtained. Michler's ketone when heated with the magnesium derivative of fluorene at 120° gave *tetramethyldi*-p-*aminodiphenyldibenzofulvene*, pale, orange-yellow crystals, m. p. 215—217°. On the addition of a drop of bromine to its chloroform solution it developed an intense violet coloration, which rapidly passed, leaving the solution colourless. The same coloration was observed on the addition of a trace of acetic acid to its alcoholic solution.

In passing from the fulvenes through the benzofulvenes to the corresponding dibenzofulvenes, there is in every case a steady diminution in colour, the dibenzofulvenes being for the most part colourless and giving pale yellow solutions. By examining the absorption spectra, quantitative comparisons have been made of the effect of introducing the four auxochrome groups, hydroxyl, methoxyl, methylenedioxy, and dimethylamino, into the phenyl group of phenylbenzofulvene. The order in general effect is

$$\cdot NMe_2 > \cdot OMe > \cdot O\cdot CH_2\cdot O\cdot > \cdot OH.$$

A comparison of the absorption spectra of diphenylbenzofulvanol, diphenyldihydrobenzofulvanol, and diphenyl*iso*benzofulvane shows: (1) that the greater the number of conjugations for the same number of double linkings the more coloured is the molecule; (2) the greater the density of the double linkings in conjugated positions the more coloured is the molecule; (3) the greater the number of ethenoid linkings the more coloured is the molecule. W. G.

The Constitution of Dypnopinacone and its Derivatives. M. DELACRE (*Ann. Chim.*, 1916, [ix], **5**, 158—193. Compare A., 1914, i, 1068).—The first part of the paper is a more detailed account of work already published (compare A., 1912, i, 30).

Dehydro-*al*-dypnopinacolin when added to acetic acid saturated with hydrogen bromide gives an *alcohol*, $C_{32}H_{26}O$, m. p. 190°, which is not acted on by sodium amalgam. With acetyl chloride it gives the *chloride*, $C_{32}H_{25}Cl$, silky needles, m. p. 196·5°. With ethyl alcohol the chloride gives no very definite product, but with methyl alcohol it yields the *ether*, $C_{32}H_{25}\cdot OMe$, vitreous needles, m. p. 191°. Bromine when added to a solution of dehydrodypnopinacolin in carbon disulphide gives *bromodehydrodypnopinacolin*, $C_{32}H_{23}OBr$, m. p. 201—202°. This bromo-derivative is not attacked by acetic acid saturated with hydrogen bromide, but it is reduced in alcoholic solution by sodium amalgam, giving an *alcohol*, $C_{32}H_{26}O$, m. p. 177—178°, isomeric with the above alcohol. It is not acted on by acetic acid or acetic anhydride, but with acetyl chloride gives a *chloride*, $C_{32}H_{25}Cl$, silky needles, m. p. 194°, from

which ethyl alcohol regenerates the original alcohol, whilst methyl alcohol gives a *methyl ether*, $C_{32}H_{25}\cdot OMe$, m. p. 189°.

Dehydro-luteo-dypnopinacolin behaves in a similar manner to its isomeride towards acetic acid saturated with hydrogen bromide, giving an *alcohol*, $C_{32}H_{26}O$, vitreous needles, m. p. 187° (corr.), isomeric with the above two alcohols, and giving with acetyl chloride a *chloride*, $C_{32}H_{25}Cl$, m. p. 217°. With ethyl alcohol, on boiling, this chloride gives its parent alcohol, but with methyl alcohol no definite product can be isolated. When brominated in carbon disulphide solution, dehydroluteodypnopinacolin yielded a *bromo*-derivative, $C_{32}H_{23}OBr$, m. p. 196—197°. This bromo-compound, unlike its isomeride described above, loses its bromine when heated with alcoholic potassium hydroxide. The bromine is also very slowly removed in this case by prolonged boiling with alcohol alone. W. G.

Benzyl Benzoate. THE EARL OF BERKELEY (T., 1916, **109**, 522—523).—See this vol., ii, 388.

Active Cinnamic Acids. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1916, 137—164).—A reply to various criticisms on the author's contention that the cinnamic acid obtained by heating this acid with tartaric acid is an optically active form. Analyses of a large number of preparations are given, together with their optical rotations. It is claimed that the admixture of possible optically active impurities, such as tartaric acid and the mono- or di-cinnamates of this acid, derived as a result of the method employed in the preparation, could be detected as a result of the analyses if they were present in sufficient amounts to impart to cinnamic acid the optical rotation actually measured. S. B. S.

Preparation of Hydroxytriarylmethanecarboxylic Acids. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P., 290601; from *J. Soc. Chem. Ind.*, 1916, **35**, 530. Compare this vol., i, 145).—Instead of an aromatic aldehyde as prescribed in the chief patent (D.R.-P., 286433), the corresponding benzal haloid or a nucleus-substitution product may be used. G. F. M.

The Structure of the Campholenic Acids. J. R. N. VAN KREGTEN (*Rec. trav. chim.*, 1916, **36**, 64—79).—Further evidence is adduced in favour of the recognised formulæ for α- and β-campholenic acids. These acids were readily hydrogenated by passing their vapours, mixed with an excess of pure, dry hydrogen, over reduced nickel at 200°, the crude product being purified in each case by conversion into its amide. α-Campholenic acid under such conditions yielded *α-dihydrocampholenamide*, m. p. 150·5° (corr.), b. p. 161—171°/13 mm., $[\alpha]_D^{16}$ +26°26′, which when warmed with alcoholic potassium hydroxide gave the free *acid*, an oily liquid, b. p. 143—144°/12 mm., $D_4^{16\cdot5}$ 0·9801, $D_4^{20\cdot5}$ 0·9773, $n_D^{21\cdot1}$ 1·46058, $[\alpha]_D^{15}$ +24°59′, giving an *ethyl* ester, b. p. 112—113°/14 mm., $D_4^{14\cdot8}$ 0·9276, $n_D^{22\cdot3}$ 1·44533, $[\alpha]_D^{15\cdot5}$ +21°49′,

and an *anilide*, m. p. 128—129° (corr.). The values of these physical constants are not in agreement with those obtained by Mahla and Tiemann (compare A., 1900, i, 507) for their dihydrocampholenic acid and its derivatives, which are said to be α-compounds.

r-β-*Dihydrocampholenamide*, similarly prepared, has m. p. 157° (corr.), and gives the free *acid*, b. p. 136—137°/10 mm., $D_4^{10.3}$ 0·9813, $D_4^{16.3}$ 0·9767, $n_D^{17.5}$ 1·45992, which yields an *ethyl* ester, b. p. 111°/13 mm., $D_4^{18.3}$ 0·9253, $n_D^{22.3}$ 1·44371, and an *anilide*, small needles, m. p. 134—134·5° (corr.).

r-β-Dihydrocampholenic acid, on treatment with phosphorus pentachloride, followed by the addition of bromine, gave when the product was poured into cold alcohol *ethyl* α-*bromo*-β-*dihydrocampholenate*, b. p. 125—130°/10 mm., which when heated with an equal weight of quinoline at 200° under reflux gave *ethyl* $\beta\Delta^1$-*campholenate*, b. p. 110—115°/12 mm.; this on saponification yielded r-$\beta\Delta^1$-*campholenic acid*, C_8H_{14}:CH·CO_2H, m. p. 94·5—95·5° (corr.). This acid when dissolved in dilute potassium hydroxide and gently warmed with 5% potassium permanganate solution gave 1:1:2-trimethyl*cyclo*pentan-3-one, identical with that prepared by Noyes (compare A., 1900, i, 202) from α-hydroxydihydro*iso*lauronolic acid and from $\alpha\beta\beta$-trimethyladipic acid. It gave a *semicarbazone*, m. p. 221·5—222°. The identity of these two ketones establishes the position of the methyl groups in the original β-campholenic acid. W. G.

Anhydrides of Tyrosine. F. GRAZIANI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 509—515. Compare A., 1915, i, 781, 869).—When tyrosine is heated with glycerol to 180° in about an hour, and maintained at 180—190° until complete solution of the tyrosine occurs, two compounds result: (1) A crystalline *anhydride*, $(C_9H_9O_2N)_x$, which separates from alcohol in slender, silky, white needles, beginning to turn brown at 260°, m. p. 278—279° (uncorr.). It yields tyrosine on hydrolysis with hydrochloric acid (D 1·10), and appears to be a cyclic anhydride, since its aqueous solution is not coloured blue when boiled with precipitated cupric oxide. With Millon's reagent, it gives a red coloration. (2) An isomeric *anhydride*, which is obtained as a dirty white, amorphous powder, turns brown at 270°, m. p. 279°, gives a red coloration with Millon's reagent, and yields tyrosine on hydrolysis. When boiled with diphenylmethane, the insoluble, amorphous anhydride is almost completely converted into the soluble, crystalline form. To a small extent the reverse change occurs on crystallisation from alcohol. T. H. P.

o-**Benzoylbenzoyl Chloride.** H. C. MARTIN (*J. Amer. Chem. Soc.*, 1916, **38**, 1142—1144).—*o*-Benzoylbenzoyl chloride has m. p. 59—60°, and not 70° as stated by earlier investigators, and whether prepared from the acid by the action of phosphorus pentachloride or by that of thionyl chloride, the same product is

obtained. Meyer (A., 1904, i, 747) obtained by the latter method a viscous oil, which he regarded as an isomeride of the crystalline form.

o-*Benzoylbenzonitrile*, $COPh\cdot C_6H_4\cdot CN$, m. p. 70°, prepared by the action of mercuric cyanide or anhydrous hydrogen cyanide on *o*-benzoylbenzoyl chloride, forms white crystals. The same product is obtained whether the chloride has been prepared with phosphorus pentachloride or with thionyl chloride.

These results do not show any evidence of a need for tautomeric formulæ for *o*-benzoylbenzoic acid (compare Meyer, *loc. cit.*, and Haller and Guyot, A., 1900, i, 170; 1901, i, 146). E. G.

The Phenylsuccinic Acid Series. III. The Optically Active Phenylsuccinic Acids and their Derivatives. HENRY WREN and HOWELL WILLIAMS (T., 1916, **109**, 572—581. Compare A., 1915, i, 406, 1061).—It was unexpectedly found that *d*-diphenylsuccinic acid is not appreciably racemised by aqueous potassium hydroxide at 100°. As this may or may not be traceable to the presence of two asymmetric carbon atoms in the molecule, a nearly related acid with only one such carbon atom, namely, *d*-phenylsuccinic acid, has been examined. The active acids and their esters and anhydrides are found to be remarkably similar to the diphenyl compounds in their behaviour.

Racemic phenylsuccinic acid was resolved by means of brucine. It was found that the salts were somewhat hydrolysed by water, so for large-scale operations alcohol was used as a solvent. The mixed salts were fractionally crystallised from alcohol, from which the salt of the *l*-acid separated first. d-*Phenylsuccinic acid* was obtained pure by recrystallisation from water, in granular aggregates or well-defined prisms, m. p. 173—174°, $[\alpha]_D^{16}$ +173·3° in acetone, +148·3° in alcohol, +174·2° in ethyl acetate, whilst the l-*acid* had m. p. 173—174°, $[\alpha]_D^{14\cdot5}$ −173·3° in acetone and $[\alpha]_D^{12\cdot5}$ −147·1° in methyl alcohol. The *d*-acid was found to suffer partial change into the anhydride when kept for a short time at its m. p., both the residual acid and the anhydride being almost completely racemised. Scarcely any racemisation occurred under treatment with aqueous potassium hydroxide at 100°.

Methyl d-*phenylsuccinate* was obtained by the action of sulphuric acid and methyl alcohol as a slightly viscous liquid, b. p. 161—162°/16 mm., $[\alpha]_D^{10}$ +142·2° in acetone (other solvents were also used); the r-*phenylsuccinate* crystallised in clusters of prisms, m. p. 57·5—58·5°. *Ethyl* d-*phenylsuccinate* was prepared in the presence of hydrogen chloride, as an oil, b. p. 166°/13 mm., $[\alpha]_D^{13}$ +103·4° in acetone; the r-*ester* had b. p. 160°/10 mm. The acids obtained on hydrolysis were considerably racemised. The *anhydrides* were obtained by cautiously warming the active acids with acetyl chloride; the *d*-form crystallised in long needles, m. p. 83·5—84·5°, $[\alpha]_D^{15}$ +100·9° in benzene; the *l*-form had the same m. p. and $[\alpha]_D^{14}$ −100·9° in benzene. The active anhydrides were found to be more stable than the racemic anhydride in moist air

(compare Dehn and Thorpe, T., 1906, **89**, 1884), but were readily hydrolysed, with slight racemisation, by boiling water.

J. C. W.

1-Chloroanthraquinone-2-carboxylic Acid. FRITZ ULLMANN and HANS BINCER (*Ber.*, 1916, **49**, 732—749).—The method which proved to be successful in the conversion of 2-chloro-3-methylanthraquinone into 2-chloroanthraquinone-3-carboxylic acid (A., 1914, i, 413) has now been applied to the oxidation of 1-chloro-2-methylanthraquinone, as offering the most economical process for the preparation of the desired acid. 1-Chloro-2-methylanthraquinone was unknown at the commencement of the work, but has since been described by Hepp and co-workers (A., 1913, i, 374). It has been found that this can be obtained, at any rate sufficiently pure for the present purpose, by chlorinating 2-methylanthraquinone by means of sulphuryl chloride and iodine in nitrobenzene solution.

The desired acid can be prepared from the nitrile. 1-*Chloroanthraquinone-2-nitrile*, $C_6H_4{<}^{CO}_{CO}{>}C_6H_2Cl\cdot CN$, is obtained, with difficulty, from the corresponding amine, as a pale yellow, crystalline powder, m. p. 248·5° (corr.), and hydrolysed by boiling with about 85% sulphuric acid.

For the chlorination of 2-methylanthraquinone, the dry substance (40 grams) was heated with iodine (4 grams), sulphuryl chloride (60 c.c.), and nitrobenzene (100 c.c.) at 100° for some hours. The yield of crude product was about 83%, but about 6% of it was apparently the ω-chloromethylanthraquinone, for an amount of hydrogen chloride equivalent to this was obtained by heating the substance with concentrated sulphuric acid. The crude material can only be purified by preparing derivatives. On boiling with aqueous alcoholic potassium sulphide, it yielded 2 : 2′-dimethyldianthraquinonyl 1 : 1′-disulphide, m. p. 247° (Gattermann, A., 1912, i, 999), and this was oxidised by concentrated nitric acid to 2-methylanthraquinone-1-sulphonic acid (*sodium* salt). A solution of this in concentrated hydrochloric acid yielded pure 1-chloro-2-methylanthraquinone when boiled with sodium chlorate. The position of the chlorine atom was proved by boiling the compound with naphthalene and copper powder, whereby 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl (Scholl, A., 1907, i, 540) resulted.

1-Chloro-2-methylanthraquinone was treated with many agents which attack chlorine. With *p*-toluenesulphonamide, potassium acetate, and a trace of copper acetate in boiling nitrobenzene, it yielded 1-p-*toluenesulphonylamino-2-methylanthraquinone*,

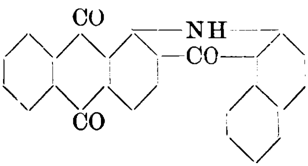
$$C_6H_4{<}^{CO}_{CO}{>}C_6H_2Me\cdot NH\cdot SO_2\cdot C_7H_7,$$

bundles of short, yellow prisms, m. p. 218° (corr.), from which 1-*amino-2-methylanthraquinone* was obtained by hydrolysis with concentrated sulphuric acid, in glistening, red crystals, m. p. 205° (corr.). 1-*Anilino-2-methylanthraquinone*, glistening, reddish-

violet needles, m. p. 229·5° (corr.), and 1-*phenoxy*-2-*methylanthraquinone*, stout, yellow crystals, m. p. 190° (corr.), were obtained by condensing the chloro-derivative with aniline and phenol respectively.

1-*Chloro*-2-*dibromomethylanthraquinone* was obtained by the action of bromine in nitrobenzene at 170°, in pale yellow needles, m. p. 179° (corr.), and converted into 1-*chloro*-2-*aldehydoanthraquinone*, $C_6H_4{<}{\substack{CO\\CO}}{>}C_6H_2Cl\cdot CHO$, by the action of concentrated sulphuric acid at 130—135°. The aldehyde crystallised in yellow needles, m. p. 198·5° (corr.), and yielded a *phenylhydrazone*, reddish-violet, microscopic needles, m. p. 269° (corr., decomp.), and an *oxime*, glistening, yellow leaflets, m. p. 232° (corr., decomp.). Oxidation to the acid was effected by means of sodium dichromate and glacial acetic acid. In all the stages the yields were excellent.

1-*Chloroanthraquinone*-2-*carboxylic acid* crystallised in pale yellow needles, m. p. 272° (corr.), and the *methyl* ester in pale yellow leaflets, m. p. 161·5° (corr.). The acid gave 1-amino- and 1-anilino-anthraquinone-2-carboxylic acids (Scholl, *Monatsh.*, 1913, **34**, 1020) on condensation with the required bases. When β-naphthylamine was applied in the same way, the 1-β-*naphthylaminoanthraquinone*-2-*carboxylic acid*, dark violet needles, m. p. 261·5° (corr.), was also accompanied by 5′ : 6′-*phthaloyl*-3 : 4-*naphthacridone* (annexed formula), which was obtained quantitatively by heating the former with acetic anhydride or acetyl chloride in nitrobenzene. The latter crystallised in brilliant red needles, m. p. 405°, and was insoluble in pyridine.



J. C. W.

Hydroxyphenylmaleic Anhydride. J. Bougault (*Compt. rend.*, 1916, **162**, 760—762. Compare A., 1914, i, 839).—*Hydroxyphenylmaleic anhydride*, $\begin{array}{l}OH\cdot C\cdot CO\\ \quad\ \ \|\\ Ph\cdot C\cdot CO\end{array}{>}O$, is readily obtained by dissolving α-cyanophenylpyruvic ester in cold concentrated sulphuric acid, pouring this solution into cold acetic acid, and slowly adding an equal volume of cold water. It crystallises from benzene in long needles, m. p. 100°, containing $1H_2O$. When dried at a low temperature, it loses this water and then has m. p. 163°. It is not stable in the presence of water, and decomposes slowly in the cold, rapidly on heating, giving phenylpyruvic acid and carbon dioxide. When heated at 100° with an alcohol, hydroxyphenylmaleic anhydride gives the corresponding ester of phenylpyruvic acid. These esters give sodium bisulphite compounds, and thus can be easily purified. They are unstable in the air, but their semicarbazones are quite stable.

Methyl phenylpyruvate semicarbazone has m. p. 196°.

Ethyl phenylpyruvate semicarbazone has m. p. 167°.

Allyl phenylpyruvate semicarbazone has m. p. 145°.

cyclo*Hexyl phenylpyruvate semicarbazone* has m. p. 145°.

Hydroxyphenylmaleic anhydride readily combines with amines and then carbon dioxide is given off rapidly in the cold, instantly on warming, and the products vary according as the amine is primary, secondary, or tertiary. Primary and secondary amines give substituted amides of phenylpyruvic acid. Aniline gives the *anilide*, m. p. 126°, β-naphthylamine the *β-naphthylamide*, m. p. 143°, and piperidine the *piperidide*, m. p. 58°, of phenylpyruvic acid. Tertiary amines give salts of phenylpyruvic acid. Thus pyridine gives *pyridine phenylpyruvate*, which is decomposed by dilute mineral acids. Ammonia gives *phenylpyruvamide*, m. p. 190°. W. G.

Diphenyldipyruvic Acid. (Mlle.) R. HEMMERLÉ (*Compt. rend.*, 1916, **162**, 758—760).—Phenylpyruvic acid or its ester condenses by aldolisation in the presence of dilute alkalis to give *diphenyldipyruvic acid*, $CH_2Ph\cdot C(OH)(CO_2H)\cdot CHPh\cdot CO\cdot CO_2H$, m. p. 194° (decomp.). When boiled with an aqueous solution of sodium acetate this acid is decomposed, giving carbon dioxide and α-keto-β-phenyl-γ-benzylbutyrolactone, m. p. 171°. If in the original condensation potassium hydrogen carbonate is the alkali used, the methyl and ethyl esters of phenylpyruvic acid give respectively the *methyl* and *ethyl* esters of *α-keto-β-phenyl-γ-benzylbutyrolactone-γ-carboxylic acid*, $CO{<}{\substack{CHPh\\CO-O}}{>}C{<}{\substack{CH_2Ph\\CO_2R}}$. These esters have respectively m. p. 160° and 140°. By passage through the enolic form they possess the property of yielding salts and ethers of the type

$$OR'\cdot C{\leqslant}{\substack{CPh-\\CO\cdot O}}{>}C{<}{\substack{CH_2Ph\\CO_2R}}.$$

The derivatives where R is an ethyl group and R′ a methyl or an ethyl group, have m. p. respectively 80° and 54°. Where R is a methyl group and R′ a methyl group the *compound* has m. p. 84°. Where R is methyl and R′ an ethyl group, the compound has not yet been obtained in a crystalline state. These ethers, when treated with hydrochloric acid in acetic acid solution, lose their carboxyl group, and yield the corresponding ethers of α-hydroxy-β-phenyl-γ-benzylbutyrolactone. W. G.

An Oxidation Product of Gallic Acid. HANNS BLEULER and ARTHUR GEORGE PERKIN (T., 1916, **109**, 529—543).—The oxidation of gallic acid by means of arsenic acid in sulphuric acid solution at temperatures above 100° has been investigated in the expectation of obtaining cœruleo-ellagic acid (T., 1911, **99**, 1442). A new colouring matter, "flavogallol," has been isolated, in addition to cœruleo-ellagic and flavogallic acids.

Flavogallol, $C_{21}H_8O_{12},4H_2O$, forms hair-like, canary-yellow needles, which decompose without melting at high temperatures, and have considerable tinctorial properties. It forms an orange-coloured, crystalline *tripotassium* salt; an *anhydrosulphate*, $C_{21}H_6O_{11},H_2SO_4$, as a glistening mass of orange-yellow prisms; a

hexa-acetate, faintly yellow, small, prismatic needles, m. p. 278—280° (decomp.); a *hexabenzoate,* small, canary-yellow prisms from benzoic anhydride, m. p. 326—328°; and an *anilide,* $C_{21}H_7O_{11}\cdot NHPh$, yellow needles, m. p. above 345°.

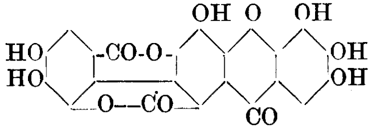
When acetylflavogallol is hydrolysed by the ethyl acetate method, the residual alcoholic liquid, on diluting with water, deposits *ethyl flavogallonate,* $C_{23}H_{14}O_{13}$, which crystallises in faintly yellow needles, m. p. above 300°, and forms an *acetyl* compound, $C_{37}H_{28}O_{20}$, m. p. 214°. The similar *methyl acetylflavogallonate,* $C_{36}H_{26}O_{20}$, forms small, prismatic needles, m. p. 181—183°. When flavogallol is added to boiling 30% potassium hydroxide containing a little alcohol the solution becomes pale and then hydrochloric acid precipitates *flavogallonic acid,* $C_{21}H_{10}O_{13}$, in pale grey needles, m. p. above 300°. Acetic anhydride or concentrated sulphuric acid in the presence of acetic acid effect the re-formation of the lactone group. Alkalis and alcohol are not the only substances which open the lactone ring in acetylflavogallol or flavogallol, for boiling acetic acid is found to act in the same way. This behaviour of alcohol and acetic acid caused much confusion at first, when they were used as possible crystallising agents. Flavogallonic acid, or flavogallol itself, is converted into *flavogallone,* $C_{20}H_{10}O_{11}$, on boiling with 50% potassium hydroxide for a few minutes. This is colourless, melts at above 340°, gives a pure blue solution with alcoholic ferric chloride, and yields an *acetate,* $C_{34}H_{24}O_{18}$, leaflets, m. p. 257—259°.

The methylation of flavogallol by means of methyl sulphate was investigated. The product was boiled with 5% alcoholic potassium hydroxide to hydrolyse any esters, and then two isomeric acids were isolated, one being less soluble than the other in alcohol. This was recognised as an *acid* of the constitution

$$C_{19}H_2O(OMe)_{10}(CO_2H)_2;$$

it crystallised in colourless prisms, m. p. 206—208°, formed a *dimethyl* ester in large plates, m. p. 128—130°, and when heated with concentrated alcoholic potassium hydroxide at 175° it was converted into the *acid,* $OH\cdot C_{19}H_2O(OMe)_9(CO_2H)_2,H_2O$, glistening leaflets, m. p. 183—184°. The more soluble isomeric *acid,* m. p. 238—240°, crystallised in large prisms with $1C_2H_5\cdot OH$, and gave a *dimethyl* ester, $C_{29}H_{32}O_{11}(CO_2Me)_2$, in large, prismatic needles, m. p. 86—87°.

Except in being yellow, forming an oxonium sulphate, and possessing strong tinctorial properties towards mordants, flavogallol is in many respects similar to ellagic acid. The annexed formula is devised for flavogallol, but cannot be regarded as satisfactory until the above methylation is more completely elucidated.



The oxidation of hexahydroxybenzophenone was also cursorily examined. This compound (D.R.-P. 49149) is readily obtained by heating gallic acid (1 part), pyrogallol (1 part), and zinc chloride

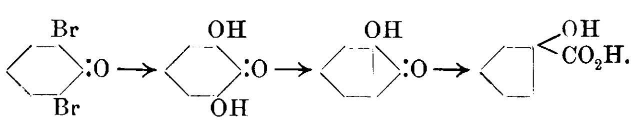
(3 parts) at 120°. It forms faintly yellow needles, m. p. 272—273°, and yields an *acetate*, $C_{25}H_{22}O_{13}$, m. p. 132°.

It was also found that acetyl groups can very generally be displaced by benzoyl groups, by heating the compound with benzoic anhydride. J. C. W.

3-Phenanthrol-4-aldehyde. JOHN WALTER SMITH (T., 1916, **109**, 568—570).—3-Phenanthrol (Werner, A., 1902, i, 437) was condensed with hydrogen cyanide under the influence of aluminium chloride, and then converted into *3-phenanthrol-4-aldehyde*, $C_{15}H_{10}O_2$, which crystallised in slender, lemon-yellow needles, m. p. 98°, b. p. 163—165°/Gaede pump. The production of a green coloration with ferric chloride, a coumarin with acetic anhydride and sodium acetate, and the conversion of the substance into morphol indicate the given constitution. *3-Hydroxyphenanthrylideneaniline*, $C_{21}H_{15}ON$, was obtained in orange-yellow crystals, m. p. 117—118°. J. C. W.

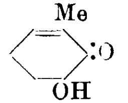
Action of Cyanogen and its Haloids on Mixed Organo-magnesium Derivatives. New Methods of Synthesis of Nitriles and Ketones. New Method of Introduction of a Halogen into an Organic Molecule. V. GRIGNARD, E. BELLET, and CH. COURTOT (*Ann. Chim.*, 1915, [ix], **3**, 28—57).—A more detailed account of work already published (A., 1911, i, 193, 292; 1912, i, 250, 623; 1914, i, 391, 945; 1915, i, 872). W. G.

A Method for the Conversion of *cyclo*Hexanones into *cyclo*-Pentanones. O. WALLACH, MATHILDE GERHARDT, and W. JESSEN (*Chem. Zentr.*, 1916, i, 365—369; from *Nachr. K. Ges. Wiss. Göttingen*, 1915, 244—263).—Many *cyclo*hexanones can be converted into *cyclo*pentanones by introducing bromine atoms into suitable positions in the ring, and treating the dibromo-derivatives thus formed with potassium hydroxide. *cyclo*Hexanone was brominated in acetic acid solution, and the dibromide obtained shaken with dilute aqueous potassium hydroxide at ordinary temperatures for an hour. From the filtered and acidified reaction mixture a *compound*, $C_6H_8O_2$ (*semicarbazone*, m. p. 230°), probably representing the intermediate product formulated below, is isolated by steam distillation. By the evaporation of the alkaline filtrate with potassium hydroxide the 1-*hydroxy*-1-*carboxylic acid*, $C_6H_{10}O_3$, m. p. 103—104°, is obtained in needles, and this on distillation with lead peroxide and sulphuric acid decomposes into *cyclo*pentanone and carbon dioxide. A *dibenzylidene* derivative, m. p. 191°, and a *semicarbazone*, m. p. 209—210° (216—217° by rapid heating), were prepared. The course of the reaction is as follows:



By a similar series of reactions methyl*cyclo*hexan-2-one gives a

dibromide, $C_7H_{10}OBr_2$, m. p. 42—43°, an intermediate product, $C_7H_{10}O_2$, of the annexed probable constitution, m. p. 62—63°, possessing strong reducing properties, and giving a violet-black coloration with ferric chloride, and a *semicarbazone*, m. p. 174—175°, and on treatment with potassium hydroxide a 2-*hydroxy*-acid,



$C_7H_{12}O_3,\frac{1}{2}H_2O$,

m. p. 74—75°. The latter on distillation with lead peroxide and sulphuric acid is converted into 1-*methyl*cyclo*pentan*-2-*one*, b. p. 140°. So also 1-methyl*cyclo*pentan-3-one is obtained both from 1-methyl*cyclo*hexan-3-one and 1-methyl*cyclo*hexan-4-one. The intermediate products in the former conversion have not yet been worked out; in the latter case the α-hydroxy-carboxylic acid, $C_7H_{12}O_3$, m. p. 99—100°, is isolated, and on distillation with lead peroxide, etc., as before, inactive methyl*cyclo*pentan-3-one is obtained. The acid would be expected to be 3-hydroxy-1-methyl-*cyclo*pentane-3-carboxylic acid, but it was not identical with that synthesised from *i*-methyl*cyclo*pentan-3-one through its cyanohydrin. 1:3-Dimethyl*cyclo*hexan-5-one gives two isomeric dibromides, $C_8H_{12}OBr_2$, m. p. 163—164° and 60—61° respectively. By treatment with alkali a *compound*, $C_8H_{12}O_2$, m. p. 71—72°, is obtained. It gives an intense coloration with ferric chloride, is strongly reducing, and on heating with alkali in an autoclave at 140° gives the *hydroxy*-acid, $C_8H_{14}O_3$, m. p. 92—93°, which on distillation with lead peroxide and sulphuric acid loses carbon dioxide and yields 1:3-*dimethyl*cyclo*pentan*-2-*one*, $C_7H_{12}O$, b. p. 152—154°, D^{17} 0·8950, n_D 1·4330, *semicarbazone*, m. p. 165—166°. From 1:3:3-trimethyl*cyclo*hexan-5-one the following compounds are obtained: dibromide, $C_9H_{14}OBr_2$, m. p. 90°, a strongly reducing intermediate *product*, $C_9H_{14}O_2$, m. p. 89—90°; a *hydroxy*-acid, $C_9H_{16}O_3$, crystallising from water in leaflets and melting at 88—89°, and finally by treatment of the latter with lead peroxide and sulphuric acid 1:3:3-*trimethyl*cyclo*pentan*-5-*one*, $C_8H_{14}O$, b. p. 159·5—161°, D^{18} 0·8785, n_D 1·4330. This ketone has a strong peppermint-like odour, gives a *semicarbazone*, m. p. 171—173·5°, and on oxidation with chromic acid a *keto*-acid, $C_8H_{14}O_3$ (*semicarbazone*, m. p. 168—169°).

Menthone is converted into dihydrocamphorphorone by treatment of its crystalline dibromide with 4% potassium hydroxide, whereby a mixture of two isomerides, $C_{10}H_{16}O_2$, is produced. They are separated by steam distillation and fractional crystallisation into an α-*compound*, $C_{10}H_{16}O_2$, m. p. 82—83°, b. p. 233—234°, crystallising in needles or prisms, and a β-*compound*, $C_{10}H_{16}O_2$, m. p. 36—38°, and more soluble in both alcohol and sodium hydroxide than the α-modification. Both compounds have reducing properties, and on heating with potassium hydroxide at 140° are converted into 1-*methyl*-3-iso*propyl*-2-*hydroxy*cyclo*pentane*-2-*carboxylic acid*, $C_{10}H_{18}O_3$, m. p. 100—101°. This on distillation in steam of its potassium salt with excess of permanganate in acid solution is decomposed into the pentacyclic ketone, *dihydrocamphorphorone* (1-*methyl*-3-iso*propyl*cyclo*pentan*-2-*one*), b. p. 184—185°, D^{19} 0·890, n_D 1·4410, *semicarbazone*, m. p. 198—199°. The *ketonic*

acid obtained by the oxidation of the ketone gives a *semicarbazone*, m. p. 163°, and an oxime, m. p. 75—76°.

Tetrahydrocarvone (carvomenthone) gives an active *dibromide*, $C_{10}H_{16}OBr_2$, m. p. 80—81°, and an inactive *dibromide*, $C_{10}H_{16}OBr_2$, m. p. 66—67°. Both these compounds give the same transformation products as the menthone dibromide above. 1-Methyl-3-*iso*propyl*cyclo*hexan-5-one gives a mixture on bromination, from which only the *α-dibromide* was isolated in a pure condition, m. p. 133—134°. The mixed bromides on shaking with aqueous potassium hydroxide give a transformation product of the β-dibromide only, the α-compound remaining unchanged. This intermediate *compound*, $C_{10}H_{16}O_2$, is isolated by steam distillation of the acidified solution, has m. p. 47—48°, and becomes oily on keeping. From the acidified liquid an *acid*, $C_{10}H_{18}O_4$, is also isolated by extraction with ether in glittering leaflets, m. p. 148—149°. It is probably a dihydroxy-acid derived from a tribromide by-product. The intermediate compound, m. p. 47—48°, is converted by potassium hydroxide at 140° into the *α-hydroxy*-acid, $C_{10}H_{18}O_3$, which on warming with lead peroxide and sulphuric acid is transformed with loss of carbon dioxide into 1-*methyl*-3-iso*propyl*cyclo*pentan*-5-*one*, $C_9H_{16}O$, b. p. 191—192°, D^{16} 0·8881, n_D 1·4430, *semicarbazone*, m. p. 150—151°, *oxime*, m. p. 91—92°. All three ketones derived from 1-methyl-3-*iso*propyl*cyclo*pentane are now accordingly known.

G. F. M.

Derivatives of 1 : 2 : 3 : 4-Tetrahydroxybenzene. G. Bargellini (*Gazzetta*, 1916, **46**, i, 249—255).—By means of the action of persulphates on phenols in alkaline solution, which has been used to transform derivatives of resorcinol into those of hydroxyquinol (Bargellini and Aureli, A., 1911, i, 855; Bargellini, A., 1913, i, 460), and to introduce a new phenolic hydroxyl into the coumarin molecule (Bargellini and Monti, A., 1915, i, 84), the author has prepared various derivatives of 1:2:3:4-tetrahydroxybenzene from derivatives of pyrogallol containing a free hydroxyl group. The new group enters in the para-position to the hydroxyl already present, when such para-position is free.

2:5-*Dihydroxy*-3:4-*dimethoxyacetophenone*,

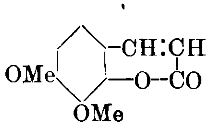
$$COMe{\cdot}C_6H(OH)_2(OMe)_2,$$

obtained by treatment of 2-hydroxy-3:4-dimethoxyacetophenone with potassium persulphate in presence of potassium hydroxide and ferrous sulphate, forms yellow needles, m. p. 119—121°, and gives a yellow solution in concentrated sulphuric acid.

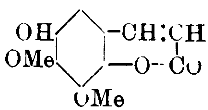
2:5-*Dihydroxy*-3:4-*dimethoxybenzophenone*,

$$COPh{\cdot}C_6H(OH)_2(OMe)_2,$$

similarly prepared from 2-hydroxy-3:4-dimethoxybenzophenone, forms small, ochre-yellow, prismatic crystals, m. p. 140—142°, and dissolves in concentrated sulphuric acid, giving a yellow solution.



7:8-*Dimethoxycoumarin* (annexed formula), prepared by the action of methyl sulphate on a solution of daphnetin in dilute aqueous potassium hydroxide, forms white needles, m. p. 119—121°.



6-*Hydroxy*-7 : 8-*dimethoxycoumarin* (annexed formula), prepared by the action of potassium persulphate on 7 : 8-dimethoxycoumarin in alkaline solution, forms yellow needles, m. p. 184°. T. H. P.

Photochemical Reduction of Benzophenone by Lactic Acid. W. D. COHEN (*Chem. Weekblad*, 1916, **13**, 596—597).—In presence of direct sunlight a mixture of benzophenone and lactic acid is converted into benzpinacone, acetaldehyde, and carbon dioxide. The author assumes that the lactic acid is first oxidised to $CH_3\cdot CO\cdot CO_2H$, which at once decomposes into the aldehyde and carbon dioxide. A. J. W.

Unsaturated Compounds in Organic Chemistry. I. Behaviour of Phenyl Cinnamylidenemethyl Ketone. MICHELE GIUA (*Gazzetta*, 1916, **46**, i, 289—297).—The equilibrium curves of various binary mixtures containing phenyl cinnamylidenemethyl ketone have been studied, and the action of bromine on the ketone investigated. The phenyl tribromodihydrocinnamylidenemethyl ketone described by Staudinger (*Chem. Zentr.*, 1903, **74**, ii, 944) appears to be a mixture of the di- and tetra-bromo-compounds, which are obtained by the author.

Phenyl tetrabromodihydrocinnamylidenemethyl ketone,

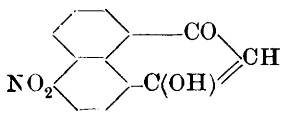
$C_{17}H_{14}OBr_4$,

forms white needles melting at 176° to a green liquid, which immediately decomposes; with concentrated sulphuric acid it gives slowly a pale red coloration.

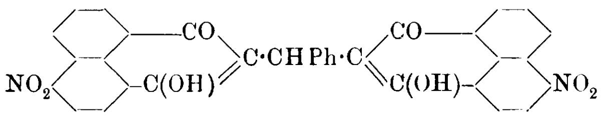
Phenyl 3-*methylstyryl ketone*, $C_6H_4Me\cdot CH\colon CH\cdot COPh$, prepared by treating an alcoholic solution of *m*-tolualdehyde and acetophenone with sodium hydroxide solution, forms pale yellow needles, m. p. 68—69°, and gives an orange-red coloration with concentrated sulphuric acid. Its *dibromide*, $C_6H_4Me\cdot CHBr\cdot CHBr\cdot COPh$, forms white needles, m. p. 127—128°, and gives a pale yellow coloration with concentrated sulphuric acid.

Phenyl cinnamylidenemethyl ketone (1 mol.) and 2 : 4 : 6-trinitrotoluene (2 mols.) form an additive compound, which crystallises in shining, dark yellow laminæ, m. p. 87·5°, and gives a dark red coloration with acetone and ammonia. With acenaphthene, phenyl cinnamylidenemethyl ketone forms no additive compound, the equilibrium curve exhibiting a eutectic point at about 67°. The systems composed of phenyl cinnamylidenemethyl ketone and (1) azobenzene and (2) β-naphthyl ethyl ether form no additive compounds, but the existence of eutectics, m. p. about 55° and 29·5° respectively, is indicated. T. H. P.

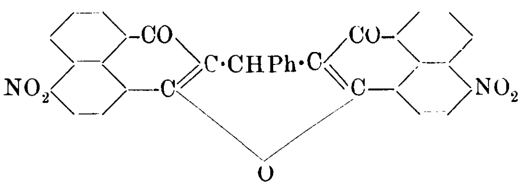
4-Nitrohydroxyketo*peri*naphthindene. E. CALDERARO (*Gazzetta*, 1916, **46**, i, 261—267. Compare A., 1915, i, 965).—6-*Nitro*-3-*hydroxy*-1-*keto*peri*naphthindene* (annexed formula), prepared by the condensation of 4-nitronaphthalic anhydride (compare Graebe and Briones, A., 1903, i, 408) with ethyl malonate in presence of fused zinc chloride, forms a



reddish-brown, crystalline crust, blackening without apparent decomposition at 300°; it dissolves in concentrated sulphuric acid, giving an intense yellow coloration. Its *ethyl* ether and *acetyl* derivative form hard, brownish-yellow, crystalline crusts, m. p. 175—176° and 156—157° respectively. With benzaldehyde in presence of pyridine it condenses to the *compound*,

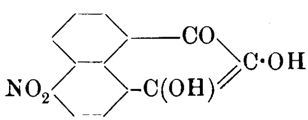


which forms a hard, shining, red, crystalline crust, m. p. 268—270° (decomp.). As is the case with dihydroxyketo*peri*naphthindenilphenylmethane (compare Errera and Cuffaro, A., 1912, i, 273), treatment of this compound with alcohol and sulphuric acid results in the elimination of a molecule of water and formation of the condensation product (annexed formula),

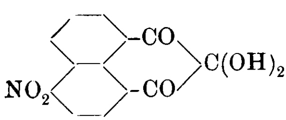


which crystallises in slender, yellow needles, not decomposing at 310°.

6-*Nitro-2 : 3-dihydroxy-1-keto*peri*naphthindene* (annexed formula), obtained in very small yield when 6-nitro-3-hydroxy-1-keto*peri*-naphthindene is treated with phenylhydrazine in alcoholic solution, forms bright red flakes, turning brown at 200°, m. p. 233° (decomp.), and reduces silver nitrate solution.



The *hydrate* of 6-*nitro*peri*naphthindantrione* (annexed formula), obtained by treating with bromine water the crude product of the action of phenylhydrazine on the nitrohydroxyketone, forms an orange-yellow, crystalline crust, and at temperatures above 100° is converted into the reddish-brown



6-*nitro*peri*naphthindan-1 : 2 : 3-trione*, $NO_2\cdot C_{10}H_5<\substack{CO \\ CO}>CO$, m. p. 210—212° (decomp.); the *phenazine* of the triketone,

$$NO_2\cdot C_{10}H_5<\substack{\text{——}C:N \\ CO\cdot C:N}>C_6H_4,$$

forms deep yellow needles, m. p. 263—265°, and the *carbamide*, $NO_2\cdot C_{10}H_5<\substack{CO \\ CO}>C<\substack{NH \\ NH}>CO$, a yellow, crystalline powder, turning brown at about 230°, m. p. 266° (decomp.). T. H. P.

Photochemical Reduction of α-Diketones. W. D. COHEN (*Chem. Weekblad*, 1916, **13**, 590—595).—Experiments on benzil and diacetyl in alcoholic solution have shown that exposure of such solutions to direct sunlight causes reduction of the ketone to pinacone and oxidation of the alcohol to aldehyde. The reaction is general for aromatic ketones and aliphatic α-diketones, but is not applicable to aliphatic monoketones. A. J. W.

Constituents of Essential Oils. Elemol, a Naturally-occurring Monocyclic Sesquiterpene Alcohol, $C_{15}H_{26}O$. F. W. SEMMLER and FUTUNG LIAO (*Ber.*, 1916, **49**, 794—798).—In an attempt to isolate elemicin from Manilla elemi oil, Schimmel & Co. obtained a solid which has now been examined. It was recognised as a sesquiterpene alcohol mixed with a little elemicin (A., 1908, i, 557), which would be difficult to purify except by conversion into an ester of much higher b. p. The *benzoate*, b. p. 214—218°/10 mm., D^{20} 1·0287, n_D 1·5378, α_D −6°, was obtained pure, and from this the alcohol, which is designated *elemol*, $C_{15}H_{26}O$, b. p. 152—156°/17 mm., D^{20} 0·9411, n_D 1·5030, α_D −5°. This was dehydrated by means of formic acid, sodium hydrogen sulphate, or zinc dust to *elemene*, $C_{15}H_{24}$, b. p. 115—117°/10 mm., D^{20} 0·8797, n_D 1·4971, which was reduced by catalytic means to *hexahydroelemene*, $C_{15}H_{30}$, b. p. 114—116°/10 mm., D^{20} 0·8450, n_D 1·4621, $[\alpha]_D$ −4·8°. Elemol itself was also reduced by catalytic means to *tetrahydroelemol*, $C_{15}H_{30}O$, b. p. 135—145°/11 mm., and this was dehydrated to *tetrahydroelemene*, b. p. 117—119°/10 mm., D^{20} 0·8659, n_D 1·4760, α_D −20·4°. The physical constants of the hydrocarbons indicated monocyclic sesquiterpenes mixed with a small amount of dicyclic sesquiterpenes, the presence of which was probably due to the unavoidable inversion which occurs during the dehydration of sesquiterpene alcohols. The compounds could not be reduced by means of sodium and alcohol, so they contained no conjugated double linkings. Elemol is the first monocyclic sesquiterpene alcohol to be found in nature or to be obtained artificially. J. C. W.

The Autoxidation of Colophony. W. FAHRION (*Chem. Zentr.*, 1916, i, 335; from *Chem. Rev. Fett-Harz-Ind.*, 1915, **22**, 97—98).—The author characterises the hypothesis of Paul (A., 1915, i, 828, 829, 1066) on the formation of α-, β-, and γ-pinic acids as baseless. G. F. M.

Analyses of Two Resinous Masses used by the Incas of South America for Embalming their Dead. L. REUTTER (*Compt. rend.*, 1916, **162**, 689—691).—The first mass analysed was found to consist of a mixture of an essence containing menthol, Tolu balsam, of resinous substances not characterised, and, in addition, mucilage of saponins, alkaloids not characterised, and sodium chloride. The second mass contained an essence with traces of menthol, Peru balsam, resins not defined, saponins, tannins and chlorides, sulphates and bromides of calcium, magnesium,

potassium, and sodium. The balsams, by reason of the cinnamic acid present, possess antiseptic and antiputrescent properties; the essences and the oleoresins keep off insects and their larvæ; the salt acts as a dehydrating agent, and the tannin closes the pores and prevents the penetration of air. W. G.

The Galactosides of the Brain. IV. The Constitution of Phrenosin and Kerasin. OTTO ROSENHEIM (*Biochem. J.*, 1916, **10**, 142—159).—Phrenosin prepared from the brain by the pyridine method of the author is identical with Thudicum's phrenosin and with substances described by other authors under the various names pseudo-cerebrin, cerebrin, cerebrone, and *d*-cerebrin. It is dextrorotatory, and furnishes on hydrolysis phrenosinic acid, $C_{25}H_{50}O_3$, sphingosine, and galactose. Kerasin, on the other hand, is lævorotatory, and yields on hydrolysis the same sugar and base as phrenosin, but the acid lignoceric, $C_{24}H_{48}O_2$, instead of phrenosinic acid. The following formula is suggested as representing the constitution of kerasin:

$$\begin{array}{l}
C_{12}H_{25}\cdot CH{:}CH\cdot CH\cdot CH(OH)\cdot CH_2\cdot NH\cdot CO\cdot C_{23}H_{47} \\
\qquad\qquad\qquad\quad | \\
\qquad\qquad\qquad\quad O \\
\qquad\qquad\qquad\quad | \\
\qquad\qquad\qquad\quad \underbrace{CH\cdot[CH\cdot OH]_2\cdot CH}_{O}\cdot CH(OH)\cdot CH_2\cdot OH
\end{array}$$

S. B. S.

The Glucosides of Digitalis Seeds and their Scission Products. H. KILIANI (*Ber.*, 1916, **49**, 701—721).—Several problems connected with the chemistry of digitalis products are dealt with.

A more expeditious method of extracting German digitalis is described (compare A., 1911, i, 139). Besides digitonin and gitonin, a new *glucoside*, granules, m. p. 225—230°, has been isolated.

An account of the purification of digitogenic acid from possible neutral admixtures is also given. Esters of this acid have been prepared, and it is found that by their formation three molecules of water are eliminated instead of two. *Methyl digitogenate*, $C_{30}H_{46}O_7$ ($C_{28}H_{44}O_8 + 2MeOH - 3H_2O$), forms long, stout columns, m. p. 137°, and the *ethyl* ester, $C_{32}H_{50}O_7,\frac{1}{4}H_2O$, has m. p. 95—96°. These could not be hydrolysed again to the acids, and, unlike the acid, they did not yield oximes. Earlier oxidations of digitogenic acid did not succeed in degrading the molecule very much. An oxidation with chromic acid is now described which resulted in the formation of a tribasic *acid*, $C_{16}H_{24}O_7,H_2O$, which crystallises in nodules of stout needles, m. p. 215—216° (decomp.), and does not reduce permanganate.

Having accumulated some pure digitonin, the author has also examined the mixture of sugars left on hydrolysis. This has been assumed to contain *d*-galactose and dextrose, and, by some, a pentose. No pentose could be detected by the author. The syrup obtained would not crystallise. It was oxidised by bromine water

and separated into *d*-galactonic acid (as the Ca-salt), a syrup soluble in alcohol (50% of the original; yet to be examined), and a sticky mass, which was oxidised by oxalic acid. The acid thus obtained formed a *phenylhydrazide*, elongated tablets, m. p. 195° (decomp.); a *calcium* salt, $(C_6H_{17}O_7)_2Ca,2H_2O$, stout columns; a *barium* salt, clusters of columns; a *zinc* salt, nodules, with $3H_2O$; and a *cadmium* salt, flat columns, with $5H_2O$. In some respects it resembles *d*-gluconic acid, but the salts differ considerably (*zinc gluconate* has $2H_2O$ and the *cadmium* salt is anhydrous). The acid does not, apparently, resemble any member of the series, but, strange to say, it yields *d*-saccharic acid on oxidation with nitric acid. J. C. W.

The Bitter Principles of Hops. I. W. Wöllmer (*Ber.*, 1916, **49**, 780—794).—A contribution to the chemistry of "humulon" or "α-hop bitter acid" or "lupulic acid."

Humulon was prepared by repeated precipitation as the lead salt from a methyl-alcoholic extract of lupulin, and finally purified by means of a *compound* with *o*-phenylenediamine,

$$C_{21}H_{30}O_5,C_6H_4(NH_2)_2,$$

which separated as a voluminous precipitate of slender, yellow needles, m. p. 115—117°, on mixing alcoholic or benzene solutions of the components. The pure humulon had m. p. 65—66·5°, $[\alpha]_D^{20}$ −212° in 96% alcohol, −232·2° in benzene, and was quite stable, odourless, and almost tasteless. It reduced ammoniacal silver oxide in the cold, and gave a deep reddish-violet colour with alcoholic ferric chloride. The presence in it of a ketonic, hydroxyl, or methoxyl group could not be proved, but the substance gave crystalline precipitates with salts of copper and lead, like a dibasic acid.

Humulon was submitted to hydrolysis by means of aqueous-alcoholic sodium hydroxide, whereby *iso*butyraldehyde (*semicarbazone*, m. p. 125—126°), acetic acid, an unsaturated acid, humulic acid, and a bitter resin (35—40% of the whole) were isolated. The unsaturated acid, $C_6H_{10}O_2$, b. p. 105°/10 mm., gave characteristic zinc, cadmium, and *silver* salts. Humulic acid, $C_{15}H_{22}O_4$, was obtained by a similar hydrolysis by Lintner and Schnell (*Zeitsch. ges. Brauw.*, 1904, **27**, 668). It is unlikely that it is a real carboxylic acid, for although it gives a deep red colour with ferric chloride it is only feebly acidic. It contains a ketonic group (*semicarbazone*, slender needles, m. p. 175°), and therefore behaves as an enol. It is unsaturated, and may be reduced by palladium and hydrogen to *dihydrohumulic acid*, $C_{15}H_{24}O_4$, flat needles and leaflets, m. p. 125—126° (*phenylhydrazone*, faintly yellow, short prisms, m. p. 133—134°).

Humulon itself was also reduced by catalytic means, whereby three molecular proportions of hydrogen were absorbed and the compound suffered fission into β-methylbutane, b. p. 26·3—27°/715 mm., and an *acid*, $C_{16}H_{24}O_5$; thus $C_{21}H_{30}O_5 + 3H_2 = C_{16}H_{24}O_5 + C_5H_{12}$. The acid formed yellow crystals, m. p. 123—125°, when titrated behaved as a monobasic acid, and yielded a *tetrabenzoate*,

$C_{16}H_{20}O_5Bz_4$, in colourless, flat prisms, m. p. 168°. Alkaline solutions of the acid very quickly absorbed oxygen and darkened in colour, whilst alcoholic solutions gave a dark blue coloration with lead acetate. A warm methyl-alcoholic solution was submitted to the action of a current of air, when a *dihydroxyquinone*, $C_{16}H_{22}O_5$, was deposited in slender, red needles, m. p. 63—64°. This formed a *lead* salt, and condensed with *o*-phenylenediamine to give a dark red *azine*, $C_{22}H_{26}O_3N_2$, m. p. 109°. J. C. W.

Reduction of Bixin. J. F. B. VAN HASSELT (*Chem. Weekblad*, 1916, **13**, 429—436).—Sodium hyposulphite reduces bixin to *α-hydrobixin*, red needles, m. p. about 200°; norbixin to *α-hydronorbixin*, large, violet, infusible crystals; and methylbixin to *α-hydromethylbixin*, violet needles, m. p. 190—192°. Titanium sesquioxide converts bixin into *β-hydrobixin*, the crystals being red by transmitted light and light violet by reflected light; norbixin into *β-hydronorbixin*, red, infusible crystals; and methylbixin into *β-hydromethylbixin*, crystals, m. p. about 170°. The α- and β-hydrobixins are converted by zinc-dust into *γ-hydrobixin*, yellow crystals, m. p. 207°. A. J. W.

Bixin. I. J. RINKES and J. F. B. VAN HASSELT (*Chem. Weekblad*, 1916, **13**, 436—442).—Experiments carried out to elucidate the constitution of bixin have shown that the ozonide of methylbixin is decomposed into certain products, partly by distillation and partly by the action of calcium carbonate. The compounds formed are formic acid; acetyl-γ-butyrolactone, m. p. 60·5°; a liquid *compound* containing 28·4% of nitrogen, and yielding a *semicarbazone*, m. p. 249°; and a *compound*, $C_8H_{10}O_3$, m. p. 85°. A. J. W.

Theory of the Process of Dyeing. PAUL PFEIFFER and FRANZ WITTKA (*Chem. Zeit.*, 1916, **40**, 357).—Further support is given, by experiments with pure amino-acids and polypeptides, to the theory of Nietzki, that the compounds of dyes with the silk or wool fibre are salts in which the amino-acids or proteins function either as acids or bases. Magenta solution decolorised by the addition of ammonia assumes again its red colour on the addition of glycine, glycylglycine, leucylglycine, etc., just as is the case on adding ammonium acetate, whereby the added acid is distributed between the ammonia and the magenta base, with the formation of the magenta salt of the amino-acid. On the other hand, salt formation occurs through the basic functions of the polypeptides, when a weak alcoholic solution of the quinonoid ethyl ester of tetrabromophenolphthalein becomes blue on the addition of glycine, etc., in the same way as the blue ammonium salt of the phenolphthalein derivative is produced on adding ammonium acetate to the above solution. The ability of polypeptides and also polyhydric alcohols to form molecular compounds with neutral salts may also account for the action of substantive dyes both on silk and wool and on cotton. G. F. M.

Autoxidation Accompanied by Opening of a Ring. K. VON AUWERS (*Ber.*, 1916, **49**, 820—827).—A specimen of 1:4-dimethylcoumaran-2-one which had been stored in a corked bottle for some months was found to have changed almost entirely into 4-acetoxy-*m*-toluic acid (Anschütz and Sieben, A., 1909, i, 730). This remarkable oxidation is assumed to be due to the addition of oxygen to the ethylene linking of the enolic form of the coumaranone, and is a good illustration of Engler's theory of autoxidation (A., 1913, i, 1200), thus:

$$C_6H_3Me\left\langle\begin{matrix}C\cdot OH\\ O\end{matrix}\right\rangle CMe + O_2 = C_6H_3Me\left\langle\begin{matrix}-C(OH)\cdot O\\ \quad\mid \qquad\quad \mid\\ O\cdot CMe-O\end{matrix}\right. = C_6H_3Me\left\langle\begin{matrix}CO_2H\\ OAc\end{matrix}\right. .$$

The oxidation was found to be much more rapid if the material was freely exposed to the air, and also proceeded when the bromine compound was exposed to moist air. Bromination also caused a still more profound change. A solution of dimethylcoumaranone in chloroform was slowly treated with its own weight of bromine at 0°, when *bromo*-p-*cresotic acid*, $OH\cdot C_6H_2MeBr\cdot CO_2H$, gradually separated in glistening needles, m. p. 200—201°.

4-Methyl-1-ethylcoumaranone was found to suffer a similar change, yielding 4-*propoxy*-m-*toluic acid*, $CO_2Et\cdot C_6H_3Me\cdot CO_2H$, in slender, lustrous needles, m. p. 139—140°, which was also prepared for comparison by acylating *p*-cresotic acid. J. C. W.

Formation of Flavonols from Benzylidenecoumaranones. K. VON AUWERS (*Ber.*, 1916, **49**, 809—819).—It has already been shown (A., 1914, i, 981) that the halogen-additive compounds of benzylidenecoumaranones are decomposed by alkalis in two ways, with the formation of monohalogenobenzylidene derivatives or flavonols, thus:

$$C_6H_4\left\langle\begin{matrix}O-\\ CO\end{matrix}\right\rangle CX\cdot CHPhX \longrightarrow C_6H_4\left\langle\begin{matrix}O-\\ CO\end{matrix}\right\rangle C\!:\!CPhX$$

or $C_6H_4\left\langle\begin{matrix}O-CPh\\ \quad\;\, \|\\ CO\cdot C\cdot OH\end{matrix}\right.$ Usually both reactions take place, but it has been recognised that various substituents influence the decomposition in one direction or the other. This has now been investigated more closely, and it is found that ortho- or para-substituents in the benzene ring with regard to the oxygen atom of the coumarone ring considerably weaken the latter system, so that flavonols arise, whilst meta-substituents make this type of decomposition difficult. Substituents in the benzene nucleus of the benzylidene grouping also affect the decomposition; two methoxy-groups or a nitro-group almost prevent the formation of flavonols.

o-*Tolyl chloroacetate*, $C_6H_4Me\cdot O\cdot CO\cdot CH_2Cl$, was prepared from *o*-cresol and the acyl chloride as a colourless oil, b. p. 127—127·6°/10 mm., and converted by treatment with aluminium chloride into 3-*chloroacetyl*-o-*cresol*, $OH\cdot C_6H_3Me\cdot CO\cdot CH_2Cl$, glistening, flat needles, m. p. 67°, volatile in superheated steam, and non-volatile 5-*chloroacetyl*-o-*cresol*, m. p. 144—145°. The former was con-

densed to 6-methylcoumaran-2-one by boiling with alcoholic sodium acetate. It crystallised in stout, lustrous prisms, m. p. 88—89° (Stoermer and Bartsch, A., 1901, i, 94, gave m. p. 102°, which was probably due to an oversight). 1-*Benzylidene*-6-*methylcoumaran*-2-*one*, $C_6H_3Me<\substack{O\\CO}>C:CHPh$, was prepared from this in long, pale yellow needles, m. p. 111·5—112·5°, and was converted into the *dibromide*, nacreous scales, m. p. 130—132°. On adding 0·1*N*-sodium hydroxide (3 mols.) to a boiling, alcoholic solution of the latter, 4-*methylflavonol*, $C_6H_3Me<\substack{O-CPh\\CO\cdot C\cdot OH}$, was obtained in very slender needles, m. p. 181—182°, which yielded an *acetate*, long, thin needles, m. p. 161—162°, and exhibited strong blue fluorescence in concentrated sulphuric acid solution.

s-m-*Xylenyl chloroacetate*, b. p. 146—147°/12 mm., readily condensed on treatment with aluminium chloride directly to 3 : 5-*dimethylcoumaran*-2-*one*, $C_6H_2Me_2<\substack{O\\CO}>CH_2$, which crystallised in lustrous, yellow needles, m. p. 75—76°, imparted a blue fluorescence to water, and gave a deep red solution in concentrated sulphuric acid. It was converted into 1-*benzylidene*-3 : 5-*dimethylcoumaran*-2-*one*, m. p. 171—172°, and this into the *dibromide*, lustrous prisms, m. p. 186°, which was almost entirely transformed into the 1-α-*bromobenzylidene* compound,

$$C_6H_2Me_2<\substack{O\\CO}>C:CPhBr,$$

flat, glistening, yellow needles, m. p. 168°, on boiling with aqueous-alcoholic sodium hydroxide. The above benzylidenedimethylcoumaranone was also chlorinated, and the *compound*,

$$C_6HClMe_2<\substack{O\\CO}>CCl\cdot CHPhCl,$$

m. p. 120°, having chlorine in either the ortho- or para-position with regard to oxygen, was found to yield some flavonol on boiling with alkali.

The *dibromide*, m. p. 182°, of 1-*p*-nitrobenzylidene-4-methylcoumaran-2-one (Fries and Finck, A., 1909, i, 42) yielded 1-α-*bromo*-p-*nitrobenzylidene*-4-*methylcoumaran*-2-*one*,

$$C_6H_3Me<\substack{O\\CO}>C:CBr\cdot C_6H_4\cdot NO_2,$$

deep yellow, felted needles, m. p. 238°, when treated with alkali. 1-m-*Nitrobenzylidene*-4-*methylcoumaran*-2-*one*, faintly yellow needles, m. p. 202°, yielded a *dibromide*, stout prisms, m. p. 193°, and the α-*bromo*-m-*nitrobenzylidene* compound, slender, yellow needles, m. p. 246—247°. The *dibromide* of the *o*-nitrobenzylidene compound (*ibid.*) formed stout prisms, m. p. 188°.

J. C. W.

Condensation of Phenol- and Dimethylanilino-thionaphthenquinones and their Coloured Derivatives. N. Dănăilă and C Cândea (*Bull. Sci. Acad. Roumaine*, 1916, **4**, 334—345).—With phenol, thiophenol, α-thionaphthol, and dimethylaniline, 2 : 3-

diketodihydrothionaphthen forms colourless condensation products analogous to those yielded by isatin (Baeyer and Lazarus, A., 1886, 155; Liebermann and Dănăilă, A., 1907, i, 976; Dănăilă, A., 1909, i, 971). When oxidised with potassium ferricyanide in alkaline solution, ketodiphenoldihydrothionaphthen yields a reddish-violet colouring matter, $C_{19}H_{14}O_3S$, which is analogous to the oxidation product of diphenolisatin, and is therefore a thio-oxyaurin. That the latter is an *o*-thio-oxyaurin of the formula $OH{\cdot}C_6H_3(SH){\cdot}C{<}^{C_6H_4{\cdot}OH}_{C_6H_4{:}O}$ or $O{:}C_6H_3(SH){:}C(C_6H_4{\cdot}OH)_2$ is confirmed by investigation of its leuco-derivative. On the other hand, the dithiophenol, $C_{20}H_{14}OS_3$, and dithio-α-naphthol derivatives, $C_{28}H_{18}OS_3$, of 2:3-thionaphthenquinone are virtually insoluble in alkali solution, and yield no coloured derivatives when oxidised in alkaline solution and no acetyl derivatives. For these condensation products the following formulæ are suggested, R representing a thiophenol or α-thionaphthol residue:

$$C_6H_4{<}^{C(SR)_2}_{\;\;\;S\;\;\;}{>}CO \quad \text{or} \quad C_6H_4{<}^{CO}_{S}{>}C(SR)_2.$$

Like dimethylanilinoisatin, the colourless dimethylanilinoketodihydrothionaphthen yields a malachite-green coloration when treated in acetic acid solution with lead peroxide.

2-*Keto*-3-*diphenoldihydro*-1-*thionaphthen*,

$$C_6H_4{<}^{C(C_6H_4{\cdot}OH)_2}_{\;\;\;\;S\;\;\;\;}{>}CO,$$

forms small, white crystals, m. p. 225—226°, and its *diacetyl* derivative, $C_{24}H_{18}O_5S$, white needles, m. p. 219°.

Diphenolthionaphthenquinone-red, or o-*thio-oxyaurin*, $C_{19}H_{14}O_3S$, forms the *leuco*-derivative, $OH{\cdot}C_6H_3(SH){\cdot}CH(C_6H_4{\cdot}OH)_2$, m. p. 192—193°.

Dithiophenolthionaphthenquinone, $C_{19}H_{14}OS_3$, forms white needles, m. p. 59—60°; *di-α-naphtholthionaphthenquinone*, $C_{28}H_{18}OS_3$, white prisms, m. p. 86°; and *dimethylanilinothionaphthenquinone*, crystals, m. p. 184·5°. T. H. P.

Dithiocoumarin. H. Simonis and Alfred Elias (*Ber.*, 1916, **49**, 763—767).—Thiocoumarin is readily obtained by distilling *o*-thiolcinnamic acid with phosphoric oxide (compare Chmelewski and Friedländer, A., 1913, i, 860). When melted with phosphorus pentasulphide it is converted into *dithiocoumarin* [2-*thiobenzothiopyrone*], $C_6H_4{<}^{CH{:}CH}_{S\text{—}CS}$, which forms deep red, pointed prisms, m. p. 104°, and has the characteristic fæcal odour of 2-thiocoumarins. It yields a *mercurichloride*, m. p. 237—239° (decomp.), and an *aurichloride*, red prisms, m. p. 208—210° (decomp.), and when boiled with alcoholic phenylhydrazine (1 mol.) and a little copper powder it gives 1-*thiocoumarinphenylhydrazone* in golden leaflets, m. p. 140°. J. C. W.

A New Synthesis of 1-Thiochromones [Benzthiopyrones] and the Preparation of 1 : 4-Dithiochromones [4-Thiobenzthiopyrones]. H. SIMONIS and ALFRED ELIAS (*Ber.*, 1916, **49**, 768—780).—When thiolbenzenes with free ortho-positions are condensed with β-ketonic esters in the presence of phosphoric oxide they readily form thiochromones (compare the oxygen analogues. A., 1913, i, 890), which may be converted into 1 : 4-dithiochromones by melting with phosphorus pentasulphide.

For the preparation of 2 : 3-*dimethylbenzthiopyrone*,

$$C_6H_4<\begin{matrix}CO\cdot CMe\\ \|\\ S-CMe\end{matrix},$$

a mixture of thiophenol and methyl methylacetoacetate is carefully added to ice-cold phosphoric oxide and then warmed at 100°. The compound forms colourless columns, m. p. 110°, is odourless and extremely stable, and absorbs bromine to form the *dibromide*, yellow granules, decomp. 132°, which is reconverted into the unsaturated substance by the action of water. It also forms an *oxime*, m. p. 62—63°, which is about 100° lower than the oxime of the corresponding oxygen chromone, and, unlike this, gives various metallic salts; *lead* salt, $(C_{11}H_{10}ONS)_2Pb$, yellow, m. p. 195°. The chromone also yields a *hydrochloride*,

$$(C_{11}H_{10}OS)_2,HCl,2H_2O,$$

silky, white needles, m. p. 98°, which is very readily hydrolysed. As in the case of the oxygen chromones, the pyrone ring is ruptured by boiling alkali hydroxides, methyl ethyl ketone and *o*-thiolbenzoic acid being formed in this instance. 2 : 3-Dimethylbenzthiopyrone is also characterised by the formation of double salts with metallic chlorides; *mercurichloride*, $X,HgCl_2$, transparent leaflets, m. p. 206°; *platinichloride*, $X_2,H_2PtCl_6,2H_2O$, orange prisms, decomp. 192°; *uranylochloride*, X_2,UO_2Cl_2, ivory-coloured needles; *aurichloride*, $X_2,HAuCl_4$, yellow powder.

4-*Thio*-2 : 3-*dimethylbenzthiopyrone*, $C_6H_4<\begin{matrix}CS\cdot CMe\\ \|\\ S-CMe\end{matrix}$, obtained by melting the 1-thio-compound with phosphorus pentasulphide, forms iridescent, reddish-brown, stout needles, m. p. 106°, and yields an *aurichloride*, $X,AuCl_3$, a brown powder, and a white *mercurichloride*, $X,HgCl_2$. When treated with bromine, sulphur bromide is obtained, and phenylhydrazine also partly removes sulphur, the phenylhydrazone which results being impure.

J. C. W.

Action of Sulphur on Indene, Hydrindene, and *cyclo*Pentadiene. II. WALTER FRIEDMANN (*Ber.*, 1916, **49**, 683—691. Compare this vol., i, 415).—The rôle of sulphur in fusing together several molecules of unsaturated hydrocarbons is further illustrated by the formation of complicated, asphalt-like derivatives from indene.

The product of the action of heat (180°) on a mixture of indene (2 mols.) and sulphur (2 atoms), after precipitation of the benzene solution with light petroleum, was a *compound*, $C_{36}H_{22}S$, a yellow

powder which sintered at 140°; half the proportion of indene resulted in the production of a black *compound*, $C_{36}H_{24}S_3$, at 180—185°, and a *compound*, $C_{27}H_{20}S$, at 210°. Indene (1 mol.) and sulphur (1 at.) were also heated at 250°, and the mass finally mixed with iron filings and raised to a red heat. On the upper part of the retort a *compound*, $C_{44 (or\ 45)}H_{24}S$, collected, in moss-green leaflets, m. p. 238°, soluble in benzene, whilst the distillate contained this and a *compound*, $C_{44 (or\ 45)}H_{32}S$, almost insoluble in benzene, which crystallised from nitrobenzene in yellow, felted needles, m. p. above 350°. The question is raised whether these are direct condensation products of indene, or whether the indene has first changed into chrysene and then into picene before condensing with sulphur, thus: $2C_{22}H_{14} + 3S = C_{44}H_{24}S + 2H_2S$. The behaviour of picene itself will be investigated.

The question of the constitution of the compound, $C_{18}H_{12}S$ (*loc. cit.*), is also discussed, that is, whether it is a sulphide or a thiophen. The sulphur is very firmly attached, and the compound does not react with ethyl iodide. It absorbs bromine, however, and is degraded by methyl sulphate, so that other possibilities have to be considered. When quickly treated with cold concentrated nitric acid, it yielded the *derivative*, $C_{18}H_{10}S(NO_2)_2$, in reddish-violet crystals, decomp. above 180°; the *dibromide*, $C_{18}H_{12}Br_2S$, crystallised in stout, salmon-red needles, m. p. 260—262°, whilst the *product*, $C_{11}H_{10}O_4S_2$, obtained by warming it with methyl sulphate, was dark green. J. C. W.

Preparation of Acidylsalicyl Derivatives of Theobromine. E. MERCK (D.R.-P. 290205; from *J. Soc. Chem. Ind.*, 1916, **35**, 557).—Acidylsalicyl [*o*-acidyloxybenzoic] derivatives of theobromine of the general formula $C_7H_7O_2N_4 \cdot CO \cdot C_6H_4 \cdot OX$ are obtained by treating metallic salts of theobromine with acidylsalicyl chlorides at moderate temperatures. The products, which are stable towards weak acids, are resolved into their components by dilute alkalis, and hence suffer decomposition in the intestines.

G. F. M.

The Morphine Alkaloids. II. J. VON BRAUN (*Ber.*, 1916, **49**, 750—763. Compare A., 1914, i, 1138).—An account of some of the reactions of derivatives of morphine and codeine, in which the *N*-methyl group is replaced by cyanogen or hydrogen.

Cyanonormorphine and cyanonorcodeine do not lend themselves to catalytic hydrogenations because of their insolubility. The dihydro-compounds can be obtained, however, by the hydrolysis of cyanodiacetyldihydronormorphine and cyanoacetyldihydronorcodeine. *Cyanodihydronorcodeine*, $C_{18}H_{20}O_3N_2$, has m. p. 213—214°, and *cyanodihydronormorphine*, $C_{17}H_{18}O_3N_2$, forms white leaflets, m. p. 291°. By prolonging the hydrolysis these may be converted into *dihydronorcodeine*, $NH{:}C_{16}H_{16}O(OH) \cdot OMe$, m. p. 194° (*hydrochloride*, m. p. 295°; *platinichloride*, stout, red needles, decomp.

245°; *nitroso*-compound, m. p. 198°), and *dihydronormorphine*, $NH:C_{16}H_{16}O(OH)_2$, m. p. 267° (*hydrochloride*, m. p. 303°; *platinichloride*, pale yellow), but these bases are more readily obtained by the catalytic reduction of norcodeine and normorphine. Dihydronorcodeine is almost physiologically inactive, whereas dihydronormorphine is equal to dihydromorphine in narcotic action, but is also very antipyretic.

The alcoholic hydroxyl groups in cyanonormorphine and cyanonorcodeine can be most easily replaced by chlorine, giving bases with reactive halogen which will lend themselves to further syntheses. Thus, the morphine base, when treated with thionyl chloride, yields *chlorocyanonormorphide*, $CN\cdot N:C_{16}H_{14}OCl\cdot OH$, decomp. 240—300°, which reacts with diethylamine to form *diethylaminocyanonormorphide*, $CN\cdot N:C_{16}H_{14}O(OH)\cdot NEt_2$, m. p. 248°. *α-Chlorocyanonorcodide*, $CN\cdot N:C_{16}H_{14}OCl\cdot OMe$, may be obtained in the same way or by treating α-chlorocodide with cyanogen bromide; it forms glistening leaflets, m. p. 187—188°, $[\alpha]_D^{20}$ $-390°$, and yields a *diethylamino*-compound, m. p. 187—188° (*platinichloride*, m. p. 248—250°). *β-Chlorocyanonorcodide*, m. p. 197—198°, $[\alpha]_D^{20}$ $-97.5°$, is obtained by heating the α-compound at its m. p. for a short time, or directly from β-chlorocodide.

Cyanonorcodeine can be nitrated, and it may be shown that the nitro-group enters the same position as it does if codeine itself is nitrated. Nitrocodeine is converted into *nitroacetylcodeine*, glistening leaflets, m. p. 203°, by warming with acetic anhydride, and this yields *nitrocyanoacetylnorcodeine*, $CN\cdot N:C_{16}H_{13}O(NO_2)(OMe)\cdot OAc$, felted needles, m. p. 222°, when treated with cyanogen bromide. When the latter is partly hydrolysed, it yields *nitrocyanonorcodeine*, m. p. 238°, which is also obtained by nitrating cyanonorcodeine, whilst prolonged hydrolysis results in the formation of *nitronorcodeine*, $NO_2\cdot C_{16}H_{13}O(NH)(OH)\cdot OMe$, in pale yellow crystals, m. p. 185° (*platinichloride*, decomp. 230—275°; *acetyl* compound, m. p. 251°; *nitroso*-compound, m. p. 236°). Nitronorcodeine cannot be obtained by nitrating norcodeine. On reduction with stannous chloride it yields *aminonorcodeine*, m. p. 221°, which forms a *triacetyl* compound, m. p. 160—162°. Nitrocyanonorcodeine likewise yields *aminocyanonorcodeine*, $CN\cdot N:C_{16}H_{13}O(NH_2)(OH)\cdot OMe$, m. p. 288° (*hydrochloride*, not molten at 300°), which is a remarkable base, for it suffers profound internal rearrangement on warming with dilute acids, and therefore will be of great interest in further investigations. It is also physiologically inactive.

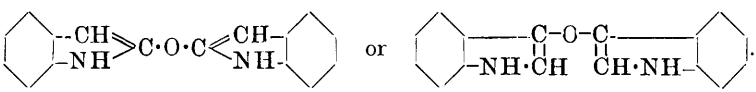
Nitrosonorcodeine may be reduced to *norcodylhydrazine*, $OH\cdot C_{16}H_{14}O(OMe):N\cdot NH_2$, by means of zinc dust and acetic acid. This is a very stable, white substance, m. p. 174°, and it forms a very sparingly soluble *hydrochloride*, with $2H_2O$, m. p. 135°, 185° (anhydrous). The important point about the hydrazine is that it is optically active; $[\alpha]_D^{20}$ $+136°$ for the base and $+116°$ for the hydrochloride. It is readily obtained, and gives very easily crystallised derivatives, so that it should be very useful in resolving racemic aldehydes and ketones. It is oxidised by mercuric oxide to the *tetrazone*, $C_{34}H_{36}O_6N_4$, m. p. 232°. J. C. W.

Preparation of Diketopyrrolidine Derivatives. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 290531; from *J. Soc. Chem. Ind.*, 1916, **35**, 558).—Diketopyrrolidines of the general formula $\begin{matrix} \text{CHR}\cdot\text{CHR}' \\ \text{CO}\text{——}\text{CO} \end{matrix}\!\!>\!\text{NR}''$, where R' and R'' are any radicles and R an acid residue, condense with ammonia at high temperatures, an amino-group entering the pyrrolidine ring, probably in the 4-position. Halogen derivatives of diketopyrrolidines react in a similar manner. The products are of therapeutic value for gout, rheumatism, etc. G. F. M.

Hydrogenation of Pyridine. ENRIQUE V. ZAPPI (*Anal. Soc. Quim. Argentina*, 1915, **3**, 433—446).—An account of the reduction of pyridine by electrolysis in alkaline and in acid solution, with and without catalysts, and by means of aluminium in alkaline and in acid solution. A. J. W.

Products of Autoxidation of Indoles: Indoxylic Ethers. BERNARDO ODDO (*Gazzetta*, 1916, **46**, i, 323—333).—Derivatives of indole readily undergo change in sunlight, this being particularly the case with 2-methylindole, which gives a yellow, crystalline compound, m. p. 208—209°, containing C 78·19%, H 6·01%, O 5·49%, and N 10·31%.

A 10% alcoholic indole solution, left for upwards of two months exposed to the light in a bottle closed by a cork perforated with four small holes, yielded a yellow *compound*, $C_{16}H_{12}ON_2$, which contracts at 220° and softens at 269°, and has the normal molecular weight in freezing acetic acid; with concentrated sulphuric acid it gives an intense violet-red coloration. Owing to the marked resistance of this compound to the action of alkali hydroxide, it is regarded as an ethereal derivative of 2- or 3-hydroxyindole, having the formula:



The latter is regarded as the more probable, since treatment of the compound with hydrochloric acid appears to yield a resinification product of indoxyl. T. H. P.

Synthesis of *iso*Quinoline Derivatives. I. ADOLF KAUFMANN and RADOŠLAV RADOSEVIĆ (*Ber.*, 1916, **49**, 675—683).—The synthesis of *iso*quinolines usually involves the preparation of phenylethylamines, which is somewhat troublesome. The authors have devised a new method which may be applied with advantage in certain cases. They condense aromatic aldehydes with acetone, reduce the products to saturated ketones, and then prepare the *syn*-oximes of these, thus: $R\cdot CHO \longrightarrow R\cdot CH{:}CH\cdot COMe \longrightarrow R\cdot CH_2\cdot CH_2\cdot COMe \longrightarrow R\cdot CH_2\cdot CH_2\cdot CMe{:}N\cdot OH$. If these are submitted to the Beckmann rearrangement, three products are commonly obtained, in varying amounts, namely, the acetyl derivative

of the amine, the methylamide of the acid, and a 1-methyl-3:4-dihydro*iso*quinoline, thus: $R\cdot CH_2\cdot CH_2\cdot NHAc$,

$$R\cdot CH_2\cdot CH_2\cdot CO\cdot NHMe, \text{ and } R<\begin{matrix}CH_2\text{-}CH_2\\ CMe:N\end{matrix}.$$

Under certain conditions and in certain cases the latter may predominate.

Piperonylideneacetone [α-3:4-methylenedioxyphenyl-Δ^{α}-buten-γ-one] may be obtained in excellent yield by adding sodium hydroxide (10 c.c. of 40% solution) to a well-stirred emulsion of piperonaldehyde (100 grams) in acetone (200 c.c.) and water (3 litres). This is quickly and almost quantitatively reduced by means of hydrogen in the presence of palladium-black and palladous chloride, giving *piperonylacetone* [α-3:4-*methylenedioxyphenylbutan*-γ-*one*], $CH_2\!:\!O_2\!:\!C_6H_3\cdot CH_2\cdot CH_2\cdot COMe$, in pearly leaflets from alcohol or massive tablets from ether, m. p. 55°, b. p. 164—165°/12 mm. The *oxime*, $C_{11}H_{13}O_3N$, m. p. 98°, is easily obtained in almost quantitative yield. This reacts readily when treated with phosphorus pentachloride in benzene solution, and the products are separated on treating the mixture with ice. The benzene layer contains the products of rearrangement, namely, *piperonylacetomethylamide* [β-3 : 4-*methylenedioxyphenylpropionomethylamide*], $CH_2\!:\!O_2\!:\!C_6H_3\cdot CH_2\cdot CH_2\cdot CO\cdot NHMe$, which crystallises readily from ether in long needles, m. p. 134°, and the *acetyl* derivative of homopiperonylamine, $CH_2\!:\!O_2\!:\!C_6H_3\cdot CH_2\cdot CH_2\cdot NHAc$, m. p. 101°, which is more soluble in ether. The aqueous layer contains the condensation product, methylnorhydrastinine, the yields of the three substances being, respectively, 20%, 45%, and 15% of the oxime. A much better yield of the *iso*quinoline base is obtained by boiling a toluene solution of the oxime with phosphoric oxide. Methylnorhydrastinine [6 : 7-methylenedioxyphenyl-1-methyl-3:4-dihydro*iso*quinoline], $CH_2\!:\!O_2\!:\!C_6H_3<\begin{matrix}CH_2\text{-}CH_2\\ CMe:N\end{matrix}$ (Decker, D.R.-P. 235358), crystallises in long, branched needles, m. p. 92°, and forms a characteristic *hydrochloride*, stout prisms, m. p. 242°, a *perchlorate*, long, broad needles, and crystalline *sulphate*. The salts exhibit a vivid blue fluorescence even in very dilute solutions.

3:4-Dimethoxybenzaldehyde was also condensed with acetone as above, and an excellent yield of α-3:4-*dimethoxyphenyl*-Δ^{α}-*buten*-γ-*one* [*methylvanillylideneacetone*], $C_6H_3(OMe)_2\cdot CH\!:\!CH\cdot COMe$, was obtained in pale yellow spikes, m. p. 91—92°. A compound, m. p. 168°, was described under this name by Francesconi and Cusmano (A., 1908, i, 802); the present authors obtained a trace of this once, and regard it as the dibenzylidene compound,

$$CO[CH\!:\!CH\cdot C_6H_3(OMe)_2]_2.$$

The reduction to α-3:4-*dimethoxyphenylbutan*-γ-*one* proceeded very quickly, and, after converting the product into the bisulphite compound, the ketone was obtained in long, soft needles, m. p. 55°, b. p. 181°/14 mm. The *oxime*, $C_{12}H_{17}O_3N$, formed well-developed crystals, m. p. 93—94°. This was heated with phosphoric oxide in toluene, and in this case practically the only

product of the reaction was 6:7-*dimethoxy*-1-*methyl*-3:4-*dihydroisoquinoline*, $C_{12}H_{15}O_2N$, which was obtained in white needles, m. p. 108°, and characterised by a *hydrochloride*, m. p. 200°, and a *picrate*, glistening, yellow needles, decomp. 205°. J. C. W.

Hydantoins. XXXVII. Synthesis of the Polypeptide-hydantoin, Phenylalanylglycinehydantoin [4-Benzylhydantoin-1-acetic Acid]. TREAT B. JOHNSON and JOSEPH SUMNER BATES (*J. Amer. Chem. Soc.*, 1916, **38**, 1087—1098).—The term polypeptide-hydantoin is applied by the authors to a cyclic derivative of a polypeptide containing a hydantoin ring which has been constructed by the union of two nitrogen atoms of the peptide with the CO-group in the form of a carbamide, and in which the characteristic grouping of the polypeptide has been preserved. As compounds of this type have not been prepared hitherto, the present investigation has been undertaken, and an account is now given of the synthesis and properties of phenylalanylglycinehydantoin (4-benzylhydantoin-1-acetic acid).

3-*Acetyl*-4-*benzylidenehydantoin*, $CO<\begin{matrix}NH-CO\\ NAc\cdot C{:}CHPh\end{matrix}$, m. p. 223° (decomp.), obtained by the action of acetic anhydride on 4-benzylidenehydantoin, forms colourless, transparent plates.

When the sodium salt of 4-benzylidenehydantoin is heated with ethyl chloroacetate in presence of potassium iodide, *ethyl* cis-4-*benzylidenehydantoin*-1-*acetate*, $CO<\begin{matrix}N(CH_2\cdot CO_2Et)\cdot CO\\ NH\text{———————}C{:}CHPh\end{matrix}$, m. p. 174°, is produced, which crystallises in rhombic prisms; a small quantity of an isomeric *substance* (probably the *trans*-modification), m. p. 158°, is formed in this reaction, and crystallises in needles. 4-*Benzylidenehydantoin*-1-*acetic acid*, m. p. 258°, forms colourless prisms, and on reduction with tin and hydrochloric acid furnishes 4-*benzylhydantoin*-1-*acetic acid* (*phenylalanylglycinehydantoin*), $CO<\begin{matrix}N(CH_2\cdot CO_2H)\cdot CO\\ NH\text{———————}CH\cdot CH_2Ph\end{matrix}$, m. p. 184—185°, which crystallises in flat prisms or rhombic plates. *Ethyl* 4-*benzylhydantoin*-1-*acetate*, m. p. 157°, crystallises in colourless needles with $1H_2O$; it can be prepared by the action of ethyl chloroacetate on 4-benzylhydantoin in presence of sodium ethoxide, by the esterification of the corresponding acid, or by the reduction of ethyl 4-benzylidenehydantoin-1-acetate with zinc dust and acetic acid or with stannous chloride. When this ester is hydrolysed with potassium hydroxide, it yields s-*phenylalanylglycinecarbamide*, $CO_2H\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot CH(CH_2Ph)\cdot CO_2H$, m. p. 176—177° (decomp.), which forms colourless prisms, and when heated at its m. p. is converted into 4-benzylhydantoin-1-acetic acid; the *dipotassium* salt of *s*-phenylalanylglycinecarbamide decomposes at 268—269°.

When ethyl benzylhydantoin-1-acetate is heated with hydrochloric acid at 140° it decomposes, with formation of phenylalanine, glycine, and carbon dioxide. E. G.

Synthesis of Mixed *cyclo*Glycylglycines by the Action of Glycerol on Mixtures of α-Amino-acids. L. C. MAILLARD (*Ann. Chim.*, 1915, [ix], **4**, 225—252. Compare A., 1915, i, 462).—Mixtures of amino-acids will condense in exactly the same way as the single amino-acids when heated together in the presence of glycerol at 170°. The author has prepared the cyclo-anhydrides from three such mixtures. Alanine and glycine when heated together in equimolecular proportions in this way yielded *r-cyclo*alanylglycine [diketomethylpiperazine] (compare Fischer and Otto, A., 1903, i, 607). Similarly, leucine when heated with an excess of glycine yielded *r-cyclo*leucylglycine (compare Fischer, A., 1905, i, 263), together with some *cyclo*glycylglycine. Similarly, leucine when heated with an excess of valine yields *r-cyclo*leucylvaline [2 : 5-diketo-6-*iso*propyl-3-*iso*butylpiperazine], m. p. 260° (compare Fischer and Scheibler, A., 1908, i, 957). W. G.

Halogenated Barbituric Acids. HEINRICH BILTZ and TONI HAMBURGER (*Ber.*, 1916, **49**, 635—655).—Although many complicated derivatives of barbituric acid have been obtained, little is known of the simpler ones, with the exception of the 5 : 5-dialkyl- and 5 : 5-dihalogeno-compounds. The monoalkyl- and especially the monohalogeno-derivatives were of particular interest to the authors, and they have succeeded in filling the gaps, with the exception of chlorodiethylbarbituric acid. Starting with alloxans, these are converted into the violuric acids, and these (or the free diethylbarbituric acid, in that particular case) are readily converted into 5 : 5-dihalogenobarbituric acids by the direct action of the halogens. The dihalogeno-acids are converted into ammonium salts of the monohalogeno-acids by treatment with aqueous ammonia (Baeyer, 1863—1864), then into potassium salts, and finally into the free acids.

A. *Barbituric Acid Series.*—Crude alloxan monohydrate, from crude uric acid, gave a 90% yield of violuric acid when warmed with aqueous hydroxylamine hydrochloride. Violuric acid gave a *compound*, $C_4H_3O_4N_3,CO(NH_2)_2$, with carbamide, in granules of colourless needles, decomp. 203—204°. A suspension of the acid in water at 30—40° was treated with chlorine, and, as soon as solution took place, the liquid was evaporated to dryness, the residue was extracted with ether, and crystallised from chloroform. 5 : 5-Dichlorobarbituric acid was obtained in 70% yield, in leaflets, m. p. 219—220° (compare Behrend, A., 1887, 129). Similarly, 5 : 5-dibromobarbituric acid was obtained in envelope-shaped tablets, m. p. 234°; yield, 80%. This was triturated with concentrated ammonia solution, when the mixture suddenly became warm, bromoform was liberated, and ammonium 5-bromobarbiturate remained. This could be recrystallised unchanged from glacial acetic acid, but boiling hydrochloric acid converted it into 5-*chlorobarbituric acid*, $C_4H_3O_3N_2Cl,2H_2O$, which could not be obtained directly from the dichloro-acid. The acid formed long, transparent needles, decomp. 280°; *potassium* salt, long, four-sided tablets. The ammonium bromobarbiturate could not be converted into the free

acid except by transforming it first into the *sodium* salt, $2H_2O$, and boiling this with 40% sulphuric acid. The acid formed elongated tablets, with $2H_2O$, m. p. 210—211° (decomp.).

B. 1-*Methylbarbituric Acid Series.*—Methylalloxan (A., 1913, i, 166) yielded 1-*methylvioluric acid*, $C_5H_5O_4N_3,H_2O$, quantitatively, in hexagonal tablets, m. p. 202—203° (decomp.), which gave a *potassium* salt, $2H_2O$, dark violet needles, and a *compound* with carbamide (1 : 1), colourless needles, m. p. 190° (decomp.). 5 : 5-*Dichloro*-1-*methylbarbituric acid*, stout prisms, m. p. 98—99° (crystals), 133° (anhydrous), and 5 : 5-*dibromo*-1-*methylvioluric acid*, stout prisms, m. p. 114° (crystals), 145—146° (anhydride), were easily prepared as above. The latter readily yielded *ammonium* 5-*bromo*-1-*methylbarbiturate*, long, slender needles, and this was converted through the potassium salt into 5-*bromo*-1-*methylbarbituric acid*, $C_5H_5O_3N_2Br,2H_2O$, rhombic tablets, m. p. 105—106°. 5-*Chloro*-1-*methylbarbituric acid*, $1H_2O$, quadratic tablets, m. p. 137°, was obtained by boiling the ammonium salt of the 5-bromo-acid with hydrochloric acid, or by boiling the dibromo- or dichloro-acid with stannous chloride and hydrochloric acid, but not by the action of ammonia on the dichloro-acid. The dibromo-acid was also reduced by means of fuming hydriodic acid and phosphonium iodide to 1-*methylbarbituric acid*, $C_5H_6O_3N_2$, elongated tablets, m. p. 132°.

C. 1 : 3-*Dimethylbarbituric Acid Series.*—Dimethylalloxan monohydrate (*ibid.*) yielded 1 : 3-dimethylvioluric acid, m. p. 124°, which gave a *compound* with carbamide (1 : 1), in long needles, m. p. 179° (decomp.). 5 : 5-Dichloro-1 : 3-dimethylbarbituric acid, m. p. 157° (Techow, A., 1895, i, 83), and 5 : 5-dibromo-1 : 3-dimethylbarbituric acid, prisms, m. p. 172—173° (Mulder, 1879), were prepared as above, and the latter was converted into 5-*bromo*-1 : 3-*dimethylbarbituric acid*, $C_6H_7O_3N_2Br$, clusters of needles, m. p. 97—99° (*ammonium* salt, long needles; *potassium* salt, long, felted needles), and into 5-*chloro*-1 : 3-*dimethylbarbituric acid*, $1H_2O$, needles or prisms, m. p. 129° (*potassium* salt, $1H_2O$, slender, flexible needles).

D. 1 : 3-*Diethylbarbituric Acid Series.*—A good yield of 1 : 3-diethylbarbituric acid was obtained by condensing malonyl chloride with diethylcarbamide. 1 : 3-Diethylvioluric acid (Sembritzki, A., 1897, i, 600) formed a molecular *compound* with carbamide, in colourless, slender prisms, m. p. 152—153° (decomp.). Dibromodiethylbarbituric acid (*ibid.*) yielded *ammonium* 5-*bromo*-1 : 3-*diethylbarbiturate*, in pale pink needles, decomp. 120°, and this gave the free *acid* on boiling with hydrochloric acid, in rosettes of very thin leaflets, m. p. 81—82°. The chloro-acid could not be obtained from the bromo-acids or salts or from the dichloro-acid.

J. C. W.

Dichlorohydurilic Acids. HEINRICH BILTZ and TONI HAMBURGER (*Ber.*, 1916, **49**, 655—662).—The basicity of hydurilic acid (5 : 5′-dibarbituric acid) was attributed to the free hydrogen atoms in the 5- and 5′-positions, because tetramethylhydurilic acid is also a strong dibasic acid (A., 1914, i, 590). In Baeyer's dichloro-

hydurilic acid the chlorine atoms must be in the 5:5′-positions, because they are not reactive like halogen atoms attached to nitrogen. Nevertheless, the acid is also strongly dibasic. It was thought that the acid would probably prove to be 5-bromobarbituric acid, but this is not the case, as direct comparisons show, and the activity must therefore be due to the imino-hydrogen. Why the acid is not consequently tetrabasic is not clear, but the formulæ for the potassium salts of hydurilic and dichlorohydurilic acids are given as follows:

$$\mathrm{CO}<\begin{matrix}\mathrm{NH{-}{-}CO}\\\mathrm{NH\cdot C(OK)}\end{matrix}\gg\mathrm{C\cdot C}\ll\begin{matrix}\mathrm{CO{-}{-}NH}\\\mathrm{C(OK)\cdot NH}\end{matrix}>\mathrm{CO} \quad \text{and}$$

$$\mathrm{CO}<\begin{matrix}\mathrm{NH{-}CO}\\\mathrm{N{:}C(OK)}\end{matrix}>\mathrm{CCl\cdot CCl}<\begin{matrix}\mathrm{CO{-}NH}\\\mathrm{C(OK){:}N}\end{matrix}>\mathrm{CO}\,.$$

The comparison of 5-chlorobarbituric acids with dichlorohydurilic acids was one of the reasons for the investigation mentioned in the preceding abstract.

5:5′-Dichlorohydurilic acid was obtained in quantitative yield by chlorinating hydurilic acid in alcohol. On treatment with stannous chloride, the original acid was regenerated. Tetramethylhydurilic acid was also chlorinated, and *5:5′-dichlorotetramethylhydurilic acid*, $C_{12}H_{12}O_6N_4Cl_2$, transparent crystals with rectangular section, m. p. 266°, was found to be devoid of any acidic properties. J. C. W.

New Derivatives of Hydurilic Acid. HEINRICH BILTZ, MYRON HEYN, and TONI HAMBURGER (*Ber.*, 1916, **49**, 662—673).—Except for a few salts, all the representatives of the hydurilic acids hitherto known are those mentioned in the preceding abstract. The authors have now obtained several new derivatives.

Although hydurilic acid can be converted into the dichloro-acid readily, it will not yield the corresponding dibromo-acid. Bromination in the presence of methyl or ethyl alcohol gives rise to *5-bromo-5′-methoxyhydurilic acid*,

$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\\mathrm{NH\cdot CO}\end{matrix}>\mathrm{CBr\cdot C(OMe)}<\begin{matrix}\mathrm{CO\cdot NH}\\\mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO},$$

which forms stout, hexagonal tablets, decomp. above 360°, or *5-bromo-5′-ethoxyhydurilic acid*, stout, elongated prisms, decomp. above 360°. This throws some light on an old reaction, namely, the fission of hydurilic acid by bromine water into dibromobarbituric acid and alloxan (Baeyer, 1863). It is supposed that a bromohydroxy-compound is formed intermediately, thus:

$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\\mathrm{NH\cdot CO}\end{matrix}>\mathrm{CBr\cdot C(OH)}<\begin{matrix}\mathrm{CO\cdot NH}\\\mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}+\mathrm{Br_2}=$$

$$\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CO}\\\mathrm{NH\cdot CO}\end{matrix}>\mathrm{CBr_2}+\mathrm{CO}<\begin{matrix}\mathrm{CO\cdot NH}\\\mathrm{CO\cdot NH}\end{matrix}>\mathrm{CO}+\mathrm{HBr}.$$

Tetramethylhydurilic acid behaves similarly. *5-Bromo-5′-methoxytetramethylhydurilic acid* forms elongated rhombic tablets, m. p. 245—247° (decomp.), and the *ethoxy*-analogue

crystallises in elongated hexagonal tablets, m. p. 199—200° (decomp.). Both are remarkably stable towards concentrated acids, but are reconverted into tetramethylhydurilic acid by means of stannous chloride. The bromine atoms could not be replaced by alkyloxyl, neither could analogous chlorine compounds be obtained. In the complete absence of water, tetramethylhydurilic acid gives with bromine in carbon tetrachloride 5:5′-*dibromohydurilic acid* in snow-white, lanceolate leaflets. This forms the above alkyloxy-compounds on treatment with alcohols, and it loses both atoms of bromine on heating at 140—180°. The product, *tetramethyldehydrohydurilic acid*,

$$CO<\begin{matrix}NMe\cdot CO\\NMe\cdot CO\end{matrix}>C:C<\begin{matrix}CO\cdot NMe\\CO\cdot NMe\end{matrix}>CO,$$

m. p. 284° (decomp.), is a highly reactive compound. It readily reacts with bromine or stannous chloride as an unsaturated substance, and combines directly with alcohols and amines at the ethylene linking. Thus with boiling methyl alcohol it forms 5-*methoxytetramethylhydurilic acid*, in stout, four-sided prisms, m. p. 284° (decomp.), whilst the 5-*ethoxy*-acid is very similar. These lose alcohol on heating, giving the dehydro-acid again, but bromine converts them into the above bromoalkyloxy-acids and chlorine into dichlorotetramethylhydurilic acid. The dehydro-acid also reacts in aqueous ammonia to form 5-*aminotetramethylhydurilic acid*, $C_{12}H_{15}O_6N_5,H_2O$, silky, rhombic leaflets, decomp. 295—300°, which forms salts, and is reduced by hydriodic acid and phosphonium iodide to 1:3-dimethyluramil and brominated in alcohol to 5:5-dibromo-1:3-dimethylbarbituric acid. 5-*Methylaminotetramethylhydurilic acid* is obtained in a very similar manner in rhombic tablets, and 5-*anilinotetramethylhydurilic acid*, m. p. 160—161° (decomp.), forms an *aniline* salt,

$$C_{18}H_{19}O_6N_5,NH_2Ph,$$

m. p. 134°. The anilino-derivative yields tetramethylhydurilic acid and aniline on reduction, thus differing from the other amino-acids. J. C. W.

Constitution of the Three Symmetrical Dinitropyrocolls. WILLIAM J. HALE and WILLIAM V. HOYT (*J. Amer. Chem. Soc.*, 1916, **38**, 1065—1071).—In an earlier paper (this vol., i, 71) it was shown that when the dinitropyrocoll obtained by Ciamician and Danesi (A., 1882, 875) by the nitration of pyrocoll is hydrolysed, it yields 3-nitropyrrole-2-carboxylic acid,

$$NH<\begin{matrix}C(CO_2H):C\cdot NO_2\\CH=\!=\!=CH\end{matrix}.$$

The conclusion was therefore drawn that the dinitropyrocoll is 3 : 3′-dinitropyrocoll, $CH<\begin{matrix}CH\text{——}N\cdot CO\cdot C:C(NO_2)\\C(NO_2):C\cdot CO\cdot N\text{——}CH\end{matrix}>CH.$ This view has now been confirmed by converting 3-nitropyrrole-2-carboxylic acid into 3:3′-dinitropyrocoll by the action of boiling acetic anhydride.

When the nitration of pyrocoll is effected by means of nitric

acid of D 1·50 and at a temperature of 4—10°, the product consists almost entirely of 3 : 3′-dinitropyrocoll, which does not melt, but decomposes at 220—225°. If, however, nitric acid of D 1·6 to 1·7 is employed, and the temperature maintained at −10° to −4°, 5 : 5′-dinitropyrocoll is produced, together with a small quantity of 4 : 4′-dinitropyrocoll.

5 : 5′-*Dinitropyrocoll*, $CH{<}\begin{matrix}C(NO_2)\cdot N\cdot CO\cdot C{=\!=\!=}CH\\ CH{=\!=\!=}C\cdot CO\cdot N\cdot C(NO_2)\end{matrix}{>}CH$, crystallises in yellow prisms; it has no definite m. p., but decomposes at 240—245°. When warmed with alkali hydroxide it suffers hydrolysis, with formation of 5-nitropyrrole-2-carboxylic acid, $NH{<}\begin{matrix}C(CO_2H){:}CH\\ C(NO_2){=}CH\end{matrix}$, m. p. 161°, which when boiled with acetic anhydride is reconverted into 5 : 5′-dinitropyrocoll.

4 : 4′-*Dinitropyrocoll*, $NO_2\cdot C{<}\begin{matrix}CH\cdot N\cdot CO\cdot C{:}CH\\ CH{:}C\cdot CO\cdot N\cdot CH\end{matrix}{>}C\cdot NO_2$, forms yellow prisms, and decomposes without melting at 315—320°; on hydrolysis it yields 4-nitropyrrole-2-carboxylic acid,

$$NH{<}\begin{matrix}C(CO_2H){:}CH\\ CH{=\!=\!=}C\cdot NO_2\end{matrix},$$

m. p. 217°, which is readily converted by acetic anhydride into the original 4 : 4′-dinitropyrocoll. E. G.

Transformation of 2 : 6-Dinitro-4-hydroxylaminotoluene into 2 : 6 : 2′ : 6′-Tetranitroazoxytoluene. K. BRAND and TH. EISENMENGER (*Ber.*, 1916, **49**, 673—674. Compare Anschütz and Zimmermann, A., 1915, i, 179).—Anschütz and Zimmermann had overlooked an earlier paper by the authors (A., 1913, i, 717), and had wrongly named the latter compound 2 : 6-dinitro-4-azoxytoluene. J. C. W.

Derivatives of Bromotolylhydrazines. FREDERICK DANIEL CHATTAWAY and GEORGE DUFOUR HODGSON (T., 1916, **109**, 582—587).—Some new derivatives of 5-bromo-*o*-tolylhydrazine and 3-bromo-*p*-tolylhydrazine are described (compare Hewitt and Pope, T., 1898, **73**, 174).

5-Bromo-*o*-tolylhydrazine yielded a *benzoyl* derivative,

$$C_6H_3MeBr\cdot NH\cdot NHBz,$$

colourless needles, m. p. 172·5°; an o-*nitrobenzoyl* compound, clusters of bright yellow, compact, flattened prisms, m. p. 179°; a m-*nitrobenzoyl* derivative, tufts of canary-yellow, slender prisms, m. p. 185° (decomp.); and a p-*nitrobenzoyl* compound, clusters of bright yellow prisms, m. p. 199° (decomp.). The corresponding derivatives of 3-bromo-*p*-tolylhydrazine were as follows: *benzoyl*, slender, hexagonal prisms, m. p. 144°; o-*nitrobenzoyl*, tufts of pale yellow, slender prisms, m. p. 177°; m-*nitrobenzoyl*, tufts of bright orange-coloured, slender prisms, m. p. 171°; and p-*nitrobenzoyl*, short, bright orange prisms, m. p. 159·5°.

The following 5-*bromo*-o-*tolylhydrazones* were prepared: of *benzaldehyde*-, unstable, pale yellow, rhombic plates, m. p. 107·5°;

o-*nitrobenzaldehyde-*, stout, ruby-red prisms, m. p. 185° (decomp.); m-*nitrobenzaldehyde-*, slender, orange needles, m. p. 216·5°; p-*nitrobenzaldehyde-*, slender, ruby-red prisms, m. p. 213°; *salicylaldehyde-*, colourless, hexagonal prisms, m. p. 105·5°; *anisaldehyde-*, unstable, elongated prisms, m. p. 95·5°; *cinnamaldehyde-*, large, orange-coloured plates, m. p. 160°; and of *pyruvic acid*, pale yellow, stout, hexagonal prisms, m. p. 180·5° (decomp.).

The corresponding 3-*bromo*-p-*tolylhydrazones* are as follow: o-*nitrobenzaldehyde-*, brilliant scarlet, rhombic plates, m. p. 178°; m-*nitrobenzaldehyde-*, stout, flattened, orange prisms, m. p. 174°; p-*nitrobenzaldehyde-*, long, stout, brilliant red prisms, m. p. 154·5°; *anisaldehyde-*, long, colourless needles, m. p. 89°; and *cinnamaldehyde-*, tufts of slender, canary-yellow plates, m. p. 120°.

Both hydrazines also condensed with citraconic and phthalic anhydrides. *Citraconyl*-5-*bromo*-o-*tolylhydrazide*,

$$C_6H_3MeBr\cdot NH\cdot N{<}\begin{matrix}CO\cdot CH\\ \quad\ \ \| \\ CO\cdot CMe\end{matrix},$$

forms deep yellow, stout prisms, m. p. 176°, and the *phthalyl* derivative pale yellow, slender prisms, m. p. 194°. *Citraconyl*-3-*bromo*-p-*tolylhydrazide* crystallises in bright yellow prisms, m. p. 102°, and the *phthalyl* compound, $C_6H_3MeBr\cdot NH\cdot N{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4$, in bright yellow, very slender needles, m. p. 162°. J. C. W.

3 : 5-Dibromo- and 3 : 5-Dichloro-phenylhydrazines. FREDERICK DANIEL CHATTAWAY and OSCAR CHARLES ELLINGTON (T., 1916, **109**, 587—593).—These hydrazines have been prepared from the corresponding anilines, and converted into typical derivatives.

3 : 5-*Dibromophenylhydrazine*, $C_6H_3Br_2\cdot NH\cdot NH_2$, crystallises in small, elongated plates, m. p. 95·5°, and is rapidly oxidised by Fehling's solution or potassium chromate to *m*-dibromobenzene. The following derivatives are described: *hydrochloride*, slender, flattened prisms, decomp. 207°; *acetyl-*, slender prisms, m. p. 198·5°; *benzoyl-*, slender plates, m. p. 206°; o-*nitrobenzoyl-*, elongated, very pale yellow plates, m. p. 204°; m-*nitrobenzoyl-*, very pale yellow prisms, m. p. 235°; p-*nitrobenzoyl-*, tufts of bright yellow, very slender prisms, m. p. 200°; and *citraconyl-*,

$$C_6H_3Br_2\cdot NH\cdot N{<}\begin{matrix}CO\cdot CH\\ \quad\ \ \| \\ CO\cdot CMe\end{matrix},$$

compact, bright yellow prisms, m. p. 155°. 3 : 5-*Dibromophenylhydrazones* of some aldehydes were also obtained, as follows: o-*nitrobenzaldehyde-*, long, bright scarlet, flattened prisms, m. p. 224° (decomp.); m-*nitrobenzaldehyde-*, clusters of bright orange, flattened prisms, m. p. 233°; p-*nitrobenzaldehyde-*, long, slender, orange prisms, which soon change in contact with the solvent (glacial acetic acid) into irregular, six-sided, red plates, m. p. 242°; *salicylaldehyde-*, pale yellow plates, m. p. 141·5°; *anisaldehyde-*, colourless prisms, m. p. 130°; and *cinnamaldehyde-*, glistening, yellow plates, m. p. 150°. The 3 : 5-*dibromophenylhydrazone* of

pyruvic acid, $C_6H_3Br_2\cdot NH\cdot N\colon CMe\cdot CO_2H$, crystallises in very pale yellow prisms, m. p. 192° (decomp.).

3:5-*Dichlorophenylhydrazine* forms elongated plates, m. p. 118°, which quickly oxidise in the air. The following derivatives are mentioned: *hydrochloride*, small, irregular plates, decomp. 190°; *acetyl-*, slender, flattened prisms, m. p. 175·5°; *benzoyl-*, clusters of plates, m. p. 221·5°; o-*nitrobenzoyl-*, very pale yellow, slender prisms, m. p. 218·5°; m-*nitrobenzoyl-*, long, slender, pale yellow prisms, m. p. 235·5°; p-*nitrobenzoyl-*, pale yellow, hair-like prisms, m. p. 196°; and *citraconyl-*, bright yellow, compact prisms, m. p. 156·5°. 3:5-*Dichlorophenylhydrazones* were obtained as follows: *benzaldehyde-*, stout, rhombic, very faintly yellow plates, m. p. 117·5°, which quickly become scarlet in the light, possibly owing to rearrangement, thus:

$$C_6H_3Cl_2\cdot NH\cdot N\colon CHPh \longrightarrow C_6H_3Cl_2\cdot N\colon N\cdot CH_2Ph;$$

o-*nitrobenzaldehyde-*, bright scarlet, very small prisms, m. p. 222°; m-*nitrobenzaldehyde-*, clusters of bright orange, minute prisms, m. p. 205°; p-*nitrobenzaldehyde-*, long, slender, orange prisms, which change in contact with the solvent into scarlet, six-sided plates, m. p. 238·5°; *salicylaldehyde-*, glistening, very faint yellow plates, m. p. 146°; *anisaldehyde-*, clusters of very slender prisms, m. p. 127°; *cinnamaldehyde-*, pale yellow, flattened prisms, m. p. 142°; and the pyruvic acid *compound*, very pale yellow, slender prisms, m. p. 192°. J. C. W.

Hydrolysis of the Anthraquinonearylhydrazones with Sulphuric Acid. G. CHARRIER (*Atti R. Accad. Sci. Torino*, 1916, **51**, 572—581).—The fact that the supposed hydroxyazo-compound, benzeneazoanthranol, is hydrolysed by nitric acid to phenylhydrazine nitrate and anthraquinone, and must therefore be regarded as anthraquinonephenylhydrazone (A., 1915, i, 904), furnishes, by analogy, an explanation of the behaviour of anthraquinone-arylhydrazones and -arylmethylhydrazones towards concentrated sulphuric acid (D 1·80—1·84). The former give deep greenish-blue and the latter emerald-green solutions in the acid, these undergoing spontaneous change in a few days and a few minutes respectively into yellow or red liquids, which are found to contain anthraquinone and the substituted hydrazine. The intensely coloured solutions of the hydroxyazo-compounds in concentrated sulphuric acid are stable and do not undergo hydrolysis, the unchanged compounds being obtained on dilution; the alkyl and acyl derivatives of the hydroxyazo-compounds are simply hydrolysed by sulphuric acid (A., 1914, i, 748). The similarity in behaviour between the arylalkylhydrazones, which are undoubtedly derived from the quinonoid form, and the arylhydrazones confirms the hydrazonic structure of the latter (compare Omarini, this vol., i, 87).

If a solution of anthraquinonephenylhydrazone in concentrated sulphuric acid is poured on to ice as soon as it assumes a wine-red colour, it yields a *compound* which forms orange-yellow needles with golden reflexion, contracting at 120—125° and decomposing at 221—222°, and contains 4·38—4·77% N. Further, the anthra-

quinone obtained by the action of sulphuric acid on anthraquinone-phenylhydrazone contains a very small proportion of a *compound*, which forms colourless, flat needles, m. p. 281—282° (decomp.), contains 13·54% N, and strongly reduces Fehling's solution.

p-Tolylmethylhydrazine, obtained by the action of sulphuric acid on anthraquinone-*p*-tolylmethylhydrazone, forms yellow leaflets, which rapidly turn brown in the air (compare Labhardt and von Zembrzuski, A., 1900, i, 125). T. H. P.

Action of Bromine on Proteins and Amino-acids. M. SIEGFRIED and H. REPPIN (*Zeitsch. physiol. Chem.*, 1915, **95**, 18—28).—The authors have estimated the amount of bromine absorbed by proteins and amino-acids under definite conditions resembling those appertaining to the estimation of phenol by Koppeschaar's method. The aliphatic amino-acids, and the aromatic amino-acids, phenylalanine and phenylglycine, do not absorb bromine under the described conditions, whilst tyrosine combines with about 5, tryptophan with 4, and histidine with rather more than 2 atoms of bromine per atom of nitrogen in the molecule. In the case of gelatin the ratio of the amount of nitrogen to the amount of bromine absorbed (N/Br) increases during hydrolysis from 15·85 to about 20. The same behaviour is observed in the case of peptone and of edestin during hydrolysis, which indicates that the complex proteins absorb more bromine than the sum of that absorbed by their products of hydrolysis. The conclusion reached by the authors is that the proteins contain complex rings capable of combining with bromine, which are broken down during the hydrolytic process. H. W. B.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. II. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1915, **95**, 263—309. Compare A., 1915, i, 324).—Oxalic, benzoic, *p*-nitrobenzoic, terephthalic, and picric acids have been isolated by the author from the products of the action of nitric acid on one or more of the proteins under investigation (*loc. cit.*). The amino-acids usually found in proteins have also been treated with nitric acid in a similar way, and the products examined. From the results it is possible to indicate the particular amino-acids in the various proteins which give rise to the acids isolated from the products of the energetic nitric acid treatment.

Under the observed conditions, all the amino-acids in proteins are capable of being oxidised to oxalic acid; from 20% to 40% of the protein is regained in this form.

Phenylalanine is the only amino-acid which yields *p*-nitrobenzoic acid on oxidation with nitric acid, and the presence of this acid among the oxidation products of a protein is conclusive evidence of the presence of phenylalanine in the original protein molecule. It is isolated in the form of its magnesium salt, which crystallises with $8H_2O$, of which seven are lost in a desiccator over sulphuric acid. The magnesium salts of benzoic and related aromatic acids

are much more soluble in water than the magnesium salt of *p*-nitrobenzoic acid.

The origin of the benzoic and terephthalic acids has not been established; neither tyrosine nor phenylalanine yields these acids on treatment with nitric acid.

The yield of picric acid is from 0·5 to 1% of the protein subjected to oxidation. Tyrosine, phenylalanine, and tryptophan are partly oxidised to picric acid under the observed experimental conditions, and therefore constitute the source of the picric acid obtained on oxidation of protein. H. W. B.

Determination of the Molecular Weight of Egg-albumin. F. VAN DER FEEN (*Chem. Weekblad*, 1916, **13**, 410—416).—From the results of determinations of the osmotic pressure of solutions of egg-albumin the author gives 26200 as the approximate molecular weight of this substance. A. J. W.

Crystallisation of Human Serum Albumin. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1915, **95**, 102—103).—Crystalline serum albumin is prepared by the customary method from the albumin in human ascitic fluid. H. W. B.

Changes in the Concentrations of Hydrogen and Hydroxyl Ions which take place in the Formation of Certain Protein Compounds. CARL L. A. SCHMIDT (*J. Biol. Chem.*, 1916, **25**, 63—79).—By a method similar to that described by Schmidt and Finger (A., 1908, ii, 802) the author measures the changes in the concentrations of hydrogen and hydroxyl ions occurring when acid and alkaline solutions of globin are titrated with solutions of other proteins and of precipitating inorganic salts. The results indicate that true protein compounds of globin are formed, some of which may precipitate at a definite acidity or alkalinity, whilst others may remain in solution. H. W. B.

Fibrin and its Relationship to Certain Problems of Biology and Colloidal Chemistry. VIII. E. HEKMA (*Biochem. Zeitsch.*, 1916, **74**, 63—92).—A discussion of the part played by alkali in the imbibition of water by fibrin. S. B. S.

Fibrin and its Relationship to Certain Problems of Biology and Colloidal Chemistry. IX. E. HEKMA (*Biochem. Zeitsch.*, 1916, **74**, 219—238).—A detailed discussion of the conditions under which a gel is formed from the alkali hydrosol of fibrin. S. B. S.

Yeast Protein. CARL NEUBERG (*Chem. Zentr.*, 1916, i, 162—163; from *Woch. Brauerei*, 1915, **32**, 317—320).—Preparations of yeast protein were obtained from two different specimens of yeast by digestion for twelve hours at the ordinary temperature, filtering, coagulating the protein in the filtrate by heating, dehydrating the coagulum by means of alcohol, and finally digesting with alcohol and ether. From the residue of the macerated yeast a further

quantity of protein was isolated by a repetition of the above process. The protein had the appearance of casein, gave the typical protein reactions, and the corresponding products from the two samples of yeast, dry yeast and under-yeast, had a very similar composition, namely, for the protein first extracted, N = 13·02% and 13·02%; S = 0·92% and 0·85%; P = 0·59% and 0·60%, and for the protein of the second extraction, N = 13·39% and 13·46%; S = 0·95% and 0·88%; and P = 0·26% and 0·27%. Calculated on its phosphorus content, protein I contained 6·2% and protein II 3% of yeast-nucleic acid. The yeast protein contained alanine and tryptophan, the first being isolated by Fischer's method as its ester, and the latter by two weeks' digestion with trypsin. Aspartic and glutamic acids were proved absent. G. F. M.

Iodoprotein. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1915, **95**, 351—352).—Snow-white iodocaseinogen is prepared by dissolving caseinogen in the necessary quantity of alkali hydroxide, cooling to 0°, adding a slight excess of alkali, and running in a cooled solution of iodine in aqueous potassium iodide, with shaking, until a slight excess of iodine is detected by means of starch. The excess of iodine quickly disappears, and must be replaced. This procedure is repeated until the excess of iodine remains after keeping for a few minutes. The solution is then dialysed at 0° until free from iodides. The iodoprotein is precipitated by dilute acetic acid and dried in a vacuum over sulphuric acid.

The snow-white powder can be preserved in the light without turning yellow. It contains about 14% of iodine, and readily dissolves in alkali. H. W. B.

The Formation of Pyridine Bases from Proteins. L. C. MAILLARD (*Compt. rend.*, 1916, **162**, 757—758).—The author considers that the work of Pictet and Chou (this vol., i, 226) on the formation of pyridine and *iso*quinoline bases from casein is in agreement with and lends support to his own previous work on the formation of humic substances (compare A., 1913, i, 1379). W. G.

Glucosamine Hydrochloride from a Mucoid Present in Ascitic Fluid. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1915, **95**, 100—101).—The mucoid is prepared from ascitic fluid, after removal of the albumin and globulin, by precipitation of the concentrated, salt-free filtrate by alcohol. After hydrolysis of the mucoid with 3% hydrochloric acid, crystals separate out on concentration, which by their crystalline form, reducing properties, caramel odour on burning, and their content of chlorine are recognised as glucosamine hydrochloride. H. W. B.

Urinoporphyrin. I. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1915, **95**, 34—60).—The porphyrin was obtained from the urine in a case of hæmatoporphyria congenita by precipitation with acetic acid, and purified by transformation into the methyl ester,

which was recrystallised from chloroform and methyl alcohol. The *methyl* ester of urinoporphyrin, $C_{48}H_{56}O_{16}N_4$, crystallises in short needles, m. p. 295°; the corresponding *ethyl* ester, $C_{55}H_{70}O_{16}N_4$, in long needles, m. p. 220°. Both esters contain seven alkyl radicles and dissolve in chloroform or glacial acetic acid, forming deep red fluorescent solutions. The substances are optically inactive. On treatment with copper acetate in acetic acid solution, the methyl ester yields a *copper* salt, $C_{48}H_{54}O_{16}N_4Cu$, fine, red needles from pyridine–acetic acid, and with ferrous acetate an *iron* salt, $C_{48}H_{54}O_{16}N_4FeCl$, prisms from chloroform and ether, which softens at about 238° and decomposes at about 280°.

On hydrolysis of the methyl ester with hydrobromic acid in glacial acetic acid solution in the cold, the free *urinoporphyrin*, $C_{41}H_{42}O_{16}N_4$, is obtained, which crystallises from pyridine–alcohol in needles containing $\frac{1}{2}C_5H_5N$. The solution in sodium hydrogen carbonate exhibits a deep red fluorescence.

The chief substance isolated from the products of the total reduction of urinoporphyrin by hydriodic acid was phonopyrrolecarboxylic acid, which was obtained in the form of the picrate, m. p. 158—159°. The basic fraction obtained from similar compounds, such as hæmin and bilirubin, by similar treatment is completely missing in the case of urinoporphyrin.

During the process of purification of the crude urinoporphyrin a second substance was isolated, insoluble in alcohol, which proved on investigation to be a *protein*, C=49·81, H=7·19, N=14·95, Cl=4·03, and S=1·07 per cent. In amount it constitutes about one-third of the crude porphyrin, and possibly it forms a definite compound with urinoporphyrin analogous to hæmoglobin.

Urinoporphyrin resembles hæmatoporphyrin in possessing the power, when subcutaneously injected into animals, of sensitising them to light, with fatal consequences. H. W. B.

Bilirubin. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1915, **95**, 78—80).—The discovery in pathological urine of what is probably a definite compound of protein and urinoporphyrin (compare preceding abstract) suggests that bilirubin also occurs in conjugated form in urine and bile. On examination, the author finds that crystalline bilirubin contains sulphur, and, after treatment with boiling acetic acid, which removes most of the sulphur, the analytical figures for the purified product agree more closely with the formula $C_{33}H_{36}O_6N_4$, which shows its relation to mesobilirubin, $C_{33}H_{40}O_6N_4$, and hemibilirubin, $C_{33}H_{44}O_6N_4$, than with the formula hitherto held ($C_{32}H_{36}O_6N_4$). H. W. B.

Constitution of Hæmin and Bilirubin. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1915, **95**, 152—160).—Adverse criticism of Piloty's theories of the constitution of hæmin and bilirubin (compare A., 1915, i, 451). H. W. B.

Hydrolysis of Yeast-Nucleic Acid with Ammonia. WALTER JONES and HILDEGARDE C. GERMANN (*J. Biol. Chem.*, 1916, **25**, 93—102).—The authors show that the triphosphonucleic acid

described by Thannhauser (A., 1914, i, 1015) is identical with guanylic acid.

When yeast-nucleic acid undergoes hydrolysis, whether by the action of ammonia or under the influence of ferments, the substance is first decomposed into two di-nucleotides, one of which contains the adenine and uracil groups, whilst the other contains the guanine and cytosine groups. The former is comparatively stable, but the latter readily undergoes hydrolysis into its component mono-nucleotides. This last decomposition occurs to a large extent when yeast-nucleic acid is heated with ammonia at 125°. At a higher temperature the products lose phosphoric acid, forming nucleosides. At 145° all the phosphoric acid is liberated and the formation of nucleosides is complete. H. W. B.

Hydrolysis of Yeast-Nucleic Acid in the Autoclave. P. A. Levene and W. A. Jacobs (*J. Biol. Chem.*, 1916, **25**, 103).—The results obtained by Jones and Germann (see preceding abstract) agree essentially with those previously obtained by the authors (A., 1911, i, 96). H. W. B.

The Optimal Reaction for Pepsin. Seizaburo Okada (*Biochem J.*, 1916, **10**, 126—129).—The optimal point is about $[H^{\cdot}] = 4 \times 10^{-2}$. Between $[H^{\cdot}] = 5{\cdot}8 \times 10^{-2}$ and $1{\cdot}7 \times 10^{-2}$ there is no considerable difference in the rate of hydrolysis. S. B. S.

Study of Certain Conditions which Affect the Activity of Proteolytic Enzymes in Wheat Flour. C. O. Swanson and E. L. Tague (*J. Amer. Chem. Soc.*, 1916, **38**, 1098—1109).—In a study of the conditions which affect the activity of the amylolytic enzymes in wheat flower (Swanson and Calvin, A., 1913, i, 1430), it was observed that the proteins of the flour were involved, and an investigation has therefore been made of the effect of certain conditions on the activity of the proteolytic enzymes. The amount of amino-nitrogen in the flour was estimated by a modification of Sörensen's formaldehyde titration method, and this method was also applied to the determination of the amount of protein hydrolysis due to the proteolytic enzymes. Owing to the number and complexity of the proteins of wheat flour, the study was limited to leucosin, the protein freely soluble in water.

The effects of adding potassium dihydrogen phosphate, dipotassium hydrogen phosphate, potassium phosphate, potassium hydroxide, potassium sulphide, ammonium chloride, calcium chloride, hydrochloric acid, egg albumin, and casein to the aqueous flour extract were determined. Ammonium and calcium chlorides have a greater accelerating effect on the rate of protein cleavage than any of the other salts. In presence of egg albumin, the rate of hydrolysis of the proteins by the proteolytic enzymes is increased, but in presence of casein no acceleration is observed.

E. G.

Adsorption of Invertase. J. M. Nelson and Edward G. Griffin (*J. Amer. Chem. Soc.*, 1916, **38**, 1109—1115).—In an

earlier paper (this vol., i, 439) it has been shown that although charcoal adsorbs invertase, the inhibition of the activity of the enzyme is not due to the adsorption, but to a change in the hydrogen-ion concentration of the reaction mixture caused by the presence of the charcoal. In continuation of this work, it has been proved that invertase is of a colloidal nature, and that the reaction between the enzyme and a sucrose solution depends on the contact of two phases. The activity of invertase is not affected whether it is adsorbed by charcoal or by a colloid, such as saponin, serum, or egg albumin, distributed uniformly through the solution. The adsorbed invertase can be displaced by a second colloid without affecting its activity. E. G.

The Optimal Conditions for the Proteoclastic Action of Taka-diastase. SEIZABURO OKADA (*Biochem. J.*, 1916, **10**, 130—136).—The optimal reaction for the proteoclastic activity is at $[H^{\cdot}] = 8{\cdot}5 \times 10^{-6}$, that is, in a medium very slightly acid. The proteoclastic ferments show considerable resistance to the action of acids, and regain their activity after neutralisation if the degree of acidity to which they have been exposed does not exceed that found in the stomachs of animals. S. B. S.

The Adsorption of Urease and its Activity in Insoluble Form. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **74**, 93—96).—Soja urease can be adsorbed by fibrin, and can still exert its activity on carbamide in the adsorbed form. The ferment is also active when it has been rendered insoluble by treatment with alcohol. S. B. S.

Ferment Immunity. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **74**, 97—104).—It has been shown by the author and Falk that urease rapidly disappears from the sera of rabbits which have been treated by injection of the ferment, whereas it can be detected for some time in the sera of untreated animals. The experiments recorded in this paper show that the disappearance of the urease from the sera of treated animals is not due to the formation of an antiferment. To exclude the action of the auxo-substances, urease on fibrin flocks was treated with serum, and the flocks were then washed with water. There was no appreciable difference in the action of the fibrin with adsorbed urease, whether it had been treated with the sera of normal animals or of animals immunised against the ferment; in both cases the serum-treated fibrin was generally slightly less active than was a fibrin which had been treated only with saline solution. S. B. S.

The Auxo-action of Amino-acids on Ureases. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **74**, 105—106).—Hippuric acid, unlike glycine, does not act as an auxo-substance to urease, but inhibits slightly its action. S. B. S.

Action of Antiseptic Substances on Ureases. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **74**, 107—108).—The action of

soja urease is not affected by toluene, but is inhibited by mustard oil and by sodium fluoride. S. B. S.

Chemical Nature of the Oxidising Ferments. A. W. VAN DER HAAR (*Arch. Sci. phys. nat.*, 1916, **41**, 312—315).—A résumé of experiments previously described (A., 1910, i, 604), from which the conclusion is drawn that the peroxydase of *Hedera* is a glucoprotein which has an oxidising action, that is accelerated catalytically by manganese. Neither the peroxydase of *Hedera* nor the peroxydase of potatoes is coagulated by boiling. In presence of proteins they are separated mechanically when the proteins are coagulated by heat. N. H. J. M.

Substituted Phenylarsinic Acid Derivatives. LES ÉTABLISSEMENTS POULENC FRÈRES (Eng. Pat., 1914, 22522; from *J. Soc. Chem. Ind.*, 1916, **35**, 557).—4-Alkylnitrosoaminophenyl-1-arsinic acids, as, for example, *4-nitrosophenylglycinearsinic acid*,

$$CO_2H\cdot CH_2\cdot N(NO)\cdot C_6H_4\cdot AsO(OH)_2,$$

are produced by treating *N*-dialkyl-*p*-aminophenylarsinic acids with nitrous acid, according to the equation: $NRR''\cdot C_6H_4\cdot AsO(OH)_2 + HONO = NO\cdot NR'\cdot C_6H_4\cdot AsO(OH)_2 + R''\cdot OH$ ($R' = CH_3\cdot$, $C_2H_5\cdot$, $\cdot CH_2\cdot CO_2H$, $\cdot CH_2\cdot CO_2Alk$, etc., and $R'' = CH_3\cdot$, $C_2H_5\cdot$, etc.). The dialkylaminophenylarsinic acids, in the above example 4-*N*-methylphenylglycinearsinic acid, required as starting materials, are produced by condensing dialkylanilines with arsenic trichloride and oxidising the product with hydrogen peroxide. The main reaction is carried out at 0°, and when the temperature has risen to 25—30° the product is poured on to ice and neutralised with sodium carbonate. 4-Nitrosophenylglycinearsinic acid is a colourless substance, decomposing at about 150°, insoluble in water and acids, but soluble in alkalis and alcohol. On treatment with strong hydrochloric acid these substances yield the corresponding *N*-monoalkyl derivatives. They may be used for the preparation of therapeutically valuable hydrazine derivatives. G. F. M.

Preparation of Soluble Alkali Salts of Mercury Compounds. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 290210; from *J. Soc. Chem. Ind.*, 1916, **35**, 557).—Instead of using the hydroxybenzoic acid compounds as prescribed in the chief patent (D.R.-P. 216267), sulphobenzoic acids or their acid or neutral alkali salts are employed. The new compounds, for example, sodium mercuri-*m*-sulphobenzoate, and sodium mercuri-*o*-sulphobenzoate, are more stable, and the action of the mercury in the organism is more gradual. Tested in equimolecular proportions with ammonium sulphide the latter compound deposits mercuric sulphide in about thirty-six hours and the former in about seventy-two hours.

G. F. M.

Physiological Chemistry.

The Experimental Physiology of High Altitudes. K. A. HASSELBALCH and J. LINDHARD (*Biochem. Zeitsch.*, 1916, **74**, 1—17).—With a diminution of the oxygen tension of the atmosphere, there is a diminution of ammonia production in the urine, and the "acidosis" observed in higher altitudes is in all probability due to the diminished production of endogenous ammonia. The ammonia production of the urine must be always considered in intimate connexion with its actual acidity, and normally the ammonia production diminishes with an increase in the value of p_H. It is just this combination of circumstances which is found in the case of mountain sickness, and acclimatisation sets in only when the value of p_H for the urine becomes normal, whilst the ammonia production remains diminished. The magnitude of the respiratory metabolism is not influenced by the oxygen tension of the atmosphere; only during mountain sickness is there an increase in the basal metabolism, and this diminishes as acclimatisation sets in.

S. B. S.

Ammonia as a Physiological Regulator of Neutrality. K. A. HASSELBALCH (*Biochem. Zeitsch.*, 1916, **74**, 18—47).—In the foregoing paper it has been shown that there is an intimate relationship between the p_H of the urine and the amount of nitrogen excreted as ammonia; the higher the p_H, the larger the percentage of nitrogen (or the total nitrogen) excreted as ammonia. If the p_H values are plotted as abscissæ and the "ammonia number" as ordinates, then it can be shown that a curve in the form of a rectangular hyperbola is obtained. The variations in the "ammonia number" (percentage of total excreted nitrogen) and the p_H are obtained by examining the urine excreted at different intervals after a meal and after various diets. The curve is different for different individuals, and shows but small variations for the same individual over prolonged periods. To characterise it, the value of the "ammonia number" corresponding with $p_H = 5{\cdot}8$ is taken, and this is designated the "reduced ammonia number." It has been found to vary between 2·2 and 5·5 for different individuals. During pregnancy, the "reduced ammonia number" is increased, and this is also the case during a fever. The "reduced ammonia number" in high altitudes or in an atmosphere of low oxygen tension is, on the other hand, diminished (*Biochem. Zeitsch.*, 1916, **74**, 48—55). S. B. S.

The "Reduced" and the "Regulated" Hydrogen Number of the Blood. K. A. HASSELBALCH (*Biochem. Zeitsch.*, 1916, **74**, 56—62).—It is proposed to retain for the term "acidosis" its original meaning, a condition in which salts of organic acids are present in the blood in abnormally large quantities. The equi-

librium between the bases and acids in the blood is determined only by the hydrion concentration = the "hydrogen number" (Michaelis). The hydrogen number of the blood under the tension of 40 mm. carbon dioxide is designated the "reduced hydrogen number," and by means of this factor the true reaction of different kinds of blood can be compared. The "regulated hydrogen number" of the blood is the final result of the regulating forces of the organism (the activity of the kidney, ammonia formation, and the respiratory activities), and is defined as the hydrogen-ion concentration of the blood under alveolar tension. It rises and falls with falling and rising stimulability of the respiratory centre.

S. B. S.

The Action of Intravenous Infusions of Hypertonic Solutions of Various Salts and Organic Substances on the Respiratory Metabolism. V. HENRIQUES (*Biochem. Zeitsch.*, 1916, **74**, 185—207).—As a measure of the respiratory exchanges, the oxygen consumption was employed, as the carbon dioxide excretion is influenced by subsidiary factors, such as the change in the hydrion concentration of the blood. The effect of the intravenous injection of strongly hypertonic solutions of salts (freezing points, $-1·85°$ to $-3·70°$) was, as a rule, insignificant. With sodium iodide and bromide, and lithium chloride, the oxygen taken up by the organism diminished by amounts varying between 7% and 16·2% of the total. The toxic action of iodine, bromine, and lithium must be considered as small. The effect of nitrate, sulphate, and phosphate of sodium was also very small, the maximal diminution of the oxygen consumed being 6·3%. The injection of hypertonic solutions of glycerol, carbamide, and sucrose caused increase in the oxygen consumption. The author considers that as the injection of these substances caused no marked alteration in the respiratory quotients, the increased consumption is not due to the combustion of the injected substances, but rather to their stimulant action on the cells, that is, to a specific dynamic effect.

S. B. S.

Physico-chemical Researches on Animal Liquids. X, ii. Variations in the Refractive Index of Blood Serum During Dialysis. G. QUAGLIARIELLO and G. BECCHINI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 428—433. Compare this vol., i, 446).—When blood serum is diluted with water, the change in the refractive index is proportional to the concentration of the diluted serum. The variation of the refractive index of serum during dialysis indicates that the latter exerts on the stable proteins present, namely, the soluble globulin and the albumin, an action which converts them from a state of true solution into one of pseudo-solution. The protein molecules are then no longer isolated, but united in more or less voluminous complexes, which remain, however, invisible under the ultramicroscope. Such an explanation accounts also for the diminution of the osmotic pressure of serum to one-sixth of its value on dialysis. T. H. P.

Effect of Surgical Procedures on the Amount of Dextrose in the Blood. ALBERT A. EPSTEIN and PAUL W. ASCHNER (*J. Biol. Chem.*, 1916, **25**, 151—162).—Almost all surgical operations performed under nitrous oxide and ether anæsthesia are followed by hyperglycæmia, in which the amount of dextrose in the blood generally increases from 30% to 50%. Intraperitoneal and extraperitoneal operations produce similar effects. Post-operative glycosuria was observed in only one case out of fifty. H. W. B.

Blood Relationship of Animals as Displayed in the Compositions of the Serum-proteins. V. Percentage of Non-proteins in the Sera of Certain Animals and Birds. R. M. JEWETT (*J. Biol. Chem.*, 1916, **25**, 21—22).—In the former articles of this series (Robertson, A., 1913, i, 122; Woolsey, A., 1913, i, 923; Thompson, A., 1915, i, 94; Briggs, A., 1915, i, 95) it was assumed that the amount of non-proteins in the blood sera of all animals was about the same. This is now found to be incorrect, and the amounts of non-protein nitrogenous matter in the sera of various animals have therefore been determined by the microrefractometric method (Robertson, A., 1915, ii, 851), and the necessary small corrections made in the figures previously given for the percentages of the various proteins in blood sera.

H. W. B.

Limit of Assimilation of Dextrose. A. E. TAYLOR and FLORENCE HULTON (*J. Biol. Chem.*, 1916, **25**, 173—175).—Quantities of dextrose up to 500 grams can be ingested by the majority of healthy adult males without producing glycosuria or hyperglycæmia. H. W. B.

The Fate of Inorganic Nitrogen in the Metabolism of the Dog. WILLIAM CALDWELL and HAROLD REX SEPTIMUS CLOTWORTHY (*Biochem. J.*, 1916, **10**, 14—25).—The experiments were undertaken primarily with the object of ascertaining whether synthesis of nitrogenous compounds can take place in the body when nitrogen is supplied in the form of ammonium salts, but the results obtained do not permit of any definite conclusion being arrived at as to this point. Various ammonium salts were added to the diet of dogs or injected subcutaneously, and the nitrogenous balance and distribution of nitrogen amongst the nitrogenous excreta of the urine were determined. The chief definite results obtained relate to the character of the nitrogenous excreta. After the administration *per os*, in the case of the organic salts, such as ammonium acetate or lactate, the added nitrogen is excreted largely in the form of carbamide. When, however, the ammonium has been given as an inorganic salt, such as the chloride, the body has to protect itself against the effects of the strong acid (hydrochloric acid), and an appreciable amount of the ammonium salt is excreted as such. When an ammonium salt is injected, the output of carbamide in the urine is appreciably increased, and there is a diminished excretion of nitrogen in the fæces. S. B. S.

Nuclein Metabolism. III. Complex Crystallised Cleavage Products of Yeast-Nucleic Acid. S. J. THANNHAUSER and G. DORFMÜLLER (*Zeitsch. physiol. Chem.*, 1915, **95**, 259—262).—The trinucleotide, triphosphonucleic acid, previously prepared by the action of human duodenal juice on yeast-nucleic acid (A., 1914, i, 1015), is also obtained by hydrolysis with ammonia in an autoclave at a temperature of 120—125° (compare Jones and Germann, this vol., i, 515). A second complex compound is also formed, and is separated by fractional precipitation with alcohol. It has acidic properties, and forms a crystalline *brucine* salt, m. p. 182—185°, which contains C=58·32, H=5·89, N=7·65, P=2·98%. H. W. B.

The Growth of Rats on Artificial Diets Containing Lactose. JACK CECIL DRUMMOND (*Biochem. J.*, 1916, **10**, 89—102).—Lactose when prepared from milk may contain traces of an impurity which acts as a growth-promoting accessory substance, which is soluble in alcohol and water, and is not destroyed when heated for six hours at a temperature of 100°. For complete growth of young animals, in addition to an adequate supply of fats, carbohydrates, and proteins, at least two accessory substances are necessary, one being soluble in fats and the other in water, and no growth is possible in any young animal when the diet of purified fats, carbohydrates, and proteins is entirely free from these. S. B. S.

Amino-acid Minimum for Maintenance and Growth, as Exemplified by Further Experiments with Lysine and Tryptophan. THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, EDNA L. FERRY, and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1916, **25**, 1—12).—Rats can be maintained at an almost constant body-weight for months on a food containing zein as its sole protein with an addition of tryptophan equal to 3% of the zein. On adding lysine and additional quantities of tryptophan to the diet the animals begin to grow, and the rate of growth increases with increasing amounts of these amino-acids furnished by the food until the normal rate is attained. In one case, a small patch of hair on the animal's back was dyed red, and this remained unchanged throughout six months of inhibited growth, until lysine was added to the diet; growth was then resumed, both in the body and the hair, with the result that the red patch speedily disappeared.

When both lysine and tryptophan are added to the zein diet the rate of growth depends on the amount of that amino-acid which is present in relatively the smallest proportion in accordance with the "law of the minimum." H. W. B.

Nature of the Dietary Deficiencies of the Wheat Embryo. E. V. McCOLLUM, NINA SIMMONDS, and WALTER PITZ (*J. Biol. Chem.*, 1916, **25**, 105—131).—The wheat embryo contains qualitatively all the factors essential for the promotion of the growth and well-being of rats, but these are not so proportioned as to constitute a satisfactory diet without several modifications. Even when these have been made, growth and reproductive power are not normal,

and it appears that the wheat embryo contains a toxic substance, associated with the fatty constituents, and therefore removed by extraction with ether. The exact nature of the toxic agent has not been ascertained. H. W. B.

Biochemical Considerations as regards Heredity; the Limits of Body Size and Length of Life. OTTO RAHN (*Biochem. Zeitsch.*, 1916, **74**, 243—247).—The author has already put forward the conception that the enzymes of the cell are thermolabile, and undergo destruction under the normal vital conditions. They are, however, replaced by synthesis, and the optimal state for vital functions is when the synthesis and destruction balance one another. It is now assumed that the enzyme synthesis takes place owing to the presence of another factor, which is also thermolabile, and probably a catalyst which is designated an agent of the second order, and this agent is itself synthesised under the influence of a thermolabile factor "of the third order." The series of agents is a finite one, and the capacity for normal exertion of vital functions will depend chiefly on the production of the last factor in the chain. The application of this conception to various biological problems is discussed. S. B. S.

Inositol of Brain and its Preparation. GORO MOMOSE (*Biochem. J.*, 1916, **10**, 120—125).—Inositol can be prepared from brain by extracting it with acetone (1 kilo. of brain to 1 litre of acetone). The acetone is then distilled off, and to the watery extract left lead acetate is first added, and then, after filtering off the precipitate thus produced, basic lead acetate. From the second lead precipitate, inositol is obtained. The inositol of human brain is identical with that of ox-brain and the ordinary *i*-inositol of plants. S. B. S.

Chemical Composition of Intestinal Mucus. I. and II. G. QUAGLIARIELLO and A. CRAIFALEANU (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 516—521, 598—600).—The principal protein present in the aqueous extract of the intestinal mucus of the pig is a nucleoprotein, for which the name *entero-nucleoprotein* is proposed. It is obtained as a greyish-green powder insoluble in water, alcohol, or ether, but soluble in dilute alkali solution, from which it is precipitated by addition of acid. It contains N, 15%; P, 0·40%, and S, 0·75%; the presence of a pentose, of purine bases, and of iron in the molecule has also been demonstrated. T. H. P.

The Carbohydrate Metabolism of the Surviving Liver of the Rabbit. J. ABELIN (*Biochem. Zeitsch.*, 1916, **74**, 248—264).—The glycogen content of the rabbit's liver does not diminish to any marked extent when it is perfused *in situ* with Tyrode's solution. The glycogen is not, furthermore, diminished when peptone is added to the perfusing fluid, and in this respect the rabbit differs from the tortoise, dog, and rat. It is supposed that there is some connexion between this fact and the known immunity of the

rabbit towards peptone. Adrenaline also fails to diminish the glycogen content of the liver when added to the perfusing fluid. The technique employed in the perfusion is described in detail.

S. B. S.

The Formation of Carbohydrates from Amino-acids in the Isolated Liver. UGO LOMBROSO and CAMILLO ARTOM (*Chem. Zentr.*, 1916, i, 167; from *Arch. Farm. Sperim.*, 1915, **20**, 211—224).—On passing diluted blood through an isolated dog's liver the glycogen decreased by 20—30% within an hour, and part was found as dextrose in the liquid, the rest being further degraded. A smaller diminution of liver glycogen was observed when the operation was carried out with Ringer's solution, and dextrose was, as before, detected in the circulatory fluid. The addition of 2 grams of dextrose to the Ringer's solution led to the combustion of the greater quantity of the mobilised glycogen. When amino-acids (1—3 grams of asparagine, leucine, alanine, glycine) were passed through the isolated liver with diluted blood, a slight increase of carbohydrate was detected in individual cases in the liver, and in other cases an increase of carbohydrate in the blood without a corresponding diminution of glycogen, indicating that the liver is capable under these conditions of converting amino-acids into carbohydrates. When Ringer's solution was used in a similar way with amino-acids, no increase in carbohydrate, either in the liver or in the circulatory fluid, could be detected, but it must be borne in mind that the formation of carbohydrate in this case is not necessarily excluded, since it might possibly have been covered by the subsequent combustion of sugar in the liver. G. F. M.

Occurrence of Arginase in the Animal Organism and its Recognition by means of the Formaldehyde Method. S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1915, **95**, 81—87).—The new method for the detection of arginase depends on the fact that whereas arginine contains only one amino-group reactive to formaldehyde, ornithine, one of the products of the action of arginase on arginine, contains two such groups. A standard solution of arginine chloride is first prepared and titrated by the Sörensen formaldehyde method. The extract of the organ (liver, for example) which is suspected to contain arginase, is divided into two equal portions and incubated with and without the addition of 5 c.c. of standard arginine solution for from six to thirty-six hours in the presence of toluene. After incubation, the difference between the amounts of *N*/10-sodium hydroxide required by the two portions on titration with formaldehyde and alkali in the usual way is equal to that required by 5 c.c. of the standard arginase solution if arginase is absent from the extract, or to twice the quantity if it is present.

The author finds by the application of this method that the liver is the only organ in the body containing arginase. Contrary to the statement of Kossel and Dakin (A., 1904, i, 840), it is absent from the kidney, thymus, and intestinal mucous membrane. Arginase

is not found at all in birds or reptiles, not even in the liver. An activation by serum of possibly inactive arginase in tissue extracts or in pressed organ juices does not occur. H. W. B.

Reaction of the Pancreas and Other Organs. J. H. LONG and F. FENGER (*J. Amer. Chem. Soc.*, 1916, **38**, 1115—1128).—The authors have shown (A., 1915, i, 1024) that the pancreas of freshly-killed animals has an acid reaction. Further quantitative work on this subject has proved that seasonal and feeding variations do not affect the reaction. Experiments have also been made on other organs. The parotid glands, the liver, and the spleen are also acid in reaction, but less so than the pancreas, whilst the bile is slightly alkaline or neutral, and the thyroid gland practically neutral.

Analysis of the press juice from the pancreas has shown that its acid reaction is due to the presence of acid phosphates (especially of potassium) and acid nucleoproteins. The alkali salts of the nucleoproteins are readily soluble in water, and are therefore present in the press juice. E. G.

The Stability of Pancreatic Lipase. DAVID HENRIQUES DE SOUZA (*Biochem. J.*, 1916, **10**, 108—114).—Glycerol extracts of pancreas retain their lipoclastic or proteoclastic activity after more than five years. Dilute extracts (1 in 3) kept with or without antiseptics for six weeks also retain their activity. Trypsin and lipase are present in concentrated and dilute glycerol extracts, the glycerol apparently inhibiting the destructive action of trypsin on lipase. S. B. S.

The Development of the Black Markings on the Wings of Pieris brassicæ. HERBERT ONSLOW (*Biochem. J.*, 1916, **10**, 26—30).—The black markings are caused by the oxidation of a colourless chromogen by tyrosinase, which is supplied from the body-lymph of the pupa by means of wing-nervures to the chromogen which had been previously deposited in the wings in the areas destined to become black. The oxidation takes place just before emergence of the fully-developed insect, as soon as atmospheric oxygen has access to the wing. S. B. S.

Amino-acids and the Formation of Silk in the Larva of Bombyx Mori. Observations and Experiments with Amino-acetic Acid. LUCIANO PIGORINI (*Chem. Zentr.*, 1916, i, 168—169; from *Arch. Farm. Sperim.*, 1915, **20**, 225—258).—To study the influence of amino-acids on the formation of silk equal quantities of silk-worms were fed on (1) dry leaves, (2) leaves moistened with water, (3) leaves sprayed with 2·5% aminoacetic acid solution, and (4) 11·4% sucrose solution. The chrysalis of the second series attained the greatest total weight, followed by the third, first, and fourth. The order of decreasing weight of dry chrysalis was fourth, first, second, and third series; and of decreasing nitrogen content of dry substance, third, first, second, and fourth series.

Even the individuals of the various series showed this constant difference in nitrogen content. The largest quantity of silk was provided by the dry substance of series 2, the least by series 4. The dry substance of the chrysalis of series 1 contained most nitrogen, followed in order by 3, 2, and 4. The silk itself, however, of series 3 contained most nitrogen, followed closely by 4. The varying manner of distribution of nitrogen between chrysalis and silk substance indicates that a nitrogen-free diet can replace nitrogen-containing substances in the chrysalis, these then being available for the synthesis of silk. The fibroin content, and also the weight and length of workable silk, was greatest in series 3, all these results pointing to the conclusion that the aminoacetic acid was absorbed and assimilated. Attempts to breed worms on leaves which were treated with a concentrated solution of aminoacetic acid revealed a considerable toxic action resulting in the ultimate death of the worms. This is attributed to decomposition products, particularly ammonia. This possibility of the formation of toxic products from amino-acids lends support to the hypothesis that silk formation is mainly a protective measure of the silk-worms, having as its object the removal of free amino-acids from the organism.

G. F. M.

The Presence and Fate of Choline in the Animal Body. A Method for the Detection of Small Amounts of Choline. M. GUGGENHEIM and W. LÖFFLER (*Biochem. Zeitsch.*, 1916, **74**, 208—218).—A method is given for converting choline into its acetyl derivative without actually isolating the base from the body fluid (urine, blood, etc.) in which it exists. The presence of the acetyl derivative can then be detected by its characteristic action on the surviving intestine of a guinea-pig, by means of which a quantity as small as 0·0000001 gram can be found. By ascertaining the maximal dilution which gives the physiological reaction, the amount of acetylcholine can be estimated with a fair amount of accuracy. One litre of urine contains normally 0·002—0·01 gram of choline, and a litre of serum contains 0·002—0·02 gram. No characteristic deviations from these numbers are found in the various pathological cases investigated. Subcutaneous injections of large quantities of choline cause no appreciable increase in the choline content of the urine; intravenous injections, on the other hand, cause a transient increase in the choline content of urine and blood; the chief part, however, is not excreted in the urine. The surviving liver only causes a small amount of change in the choline when this base is perfused through it. Commercial ovolecithin preparations contain minute quantities of choline; a scission of the base does not take place when the lecithin is exposed to Röntgen rays.

S. B. S.

The Distribution of Iodine Compounds in the Organism and its Relationship to their Constitution. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **74**, 123—130).—The following substances were administered in quantities containing equivalent amounts of

iodine (0·41 gram per kilo. of body-weight) to rabbits: di-iodobrassidic acid and its calcium salt and ethyl ester, calcium iodobehenate (sajodin), and di-iodotariric acid (iodostarin). The animals were killed after twenty-four hours, and the iodine was then estimated colorimetrically in portions of the lungs, liver, blood, and fat, and the results were tabulated as the number of mg. of iodine per gram of dried weight. It was found that the fat contained relatively large quantities of iodine when the salts of the acids had been administered, but not after administration of the free acids themselves. S. B. S.

Physico-chemical Investigations on Animal Liquids. XI. Chemical Reaction of the Bile. G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 536—538).—For various samples of bile procured by means of an incision of the gall-bladder, divergent results were obtained for the reaction, the value of $[H^{\cdot}] \times 10^7$ varying from 0·129 to 2·090 (A., 1911, ii, 1114). With bile direct from the liver the results obtained are more constant, and vary only between 0·130 and 0·211, except in one instance, when the low value 0·073 was found. These numbers are in better accord with those given by other animal liquids, dog's blood, for example, giving the number 0·22. T. H. P.

Amount of Acetone in Milk. N. O. ENGFELDT (*Zeitsch. physiol. Chem.*, 1915, **95**, 337—350).—The proteins of milk are first removed by tannic acid. The acetone is then distilled from the filtrate, and estimated either by the iodometric or the author's colorimetric method (A., 1915, ii, 591). The amount of acetone in mg. per litre in the milk of various animals is as follows: cow, 1·45—2·42; horse, 0·48—0·97; sheep, 0·48—0·68; goat, 0·97—1·45; human, 0·48—1·16. H. W. B.

Synthesis of Hippuric Acid in the Animal Organism. III. Excretion of Uric Acid in Man after Ingestion of Sodium Benzoate. HOWARD B. LEWIS and WALTER G. KARR (*J. Biol. Chem.*, 1916, **25**, 13—20).—During the first four hours after the administration of sodium benzoate the elimination of hippuric acid is at a maximum, whilst the excretion of uric acid is markedly diminished. A corresponding increase in the rate of uric acid excretion does not subsequently occur. The authors suggest that the glycine required for the transformation of benzoic into hippuric acid in the body is furnished in part by the products of decomposition of uric acid. The diminished elimination of uric acid is not due to a toxic action of the benzoate, because the ingestion of hippurates does not produce a similar effect. Moreover, the amount of creatinine excreted after the ingestion of sodium benzoate remains constant. H. W. B.

The Excretion of Magnesium by the Urine. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **74**, 131—133).—The magnesium and calcium excreted in the urine of a patient treated for tetanus by

injection of 25% solutions of magnesium sulphate were estimated. During the treatment the magnesium was excreted in much larger amounts than the calcium. Conditions as regards calcium and magnesium excretion rapidly became normal after the treatment with magnesium salts had ceased. S. B. S.

The Isolation of Methylguanidine by the Silver Method. ARTHUR JAMES EWINS (*Biochem. J.*, 1916, **10**, 103—107).—The author has succeeded in isolating from the urine of typhoid patients methylguanidine in quantities larger than those stated to have been found in normal urine. Subsequently he found similarly large amounts in normal urine, and he now shows that it is probable that the base is derived from creatinine (or creatine) during the precipitation of the silver salt of bases, which is brought down in the presence of alkalis. Methylguanidine can be obtained directly from creatinine when the silver method is applied to the latter base, the amount of the former obtainable depending on the temperature, time of action of the alkali, etc. S. B. S.

Anaphylaxis by Diglycylglycine. EDGARD ZUNZ and (MLLE.) DIAKONOFF (*Biochem. J.*, 1910, **16**, 160—168).—It is possible to render rabbits anaphylactic by three injections of diglycylglycine at intervals of seven days, although more marked effect is produced by a larger number of injections. Anaphylactic shock produced by injection of the peptide or of fresh horse serum into animals thus sensitised shows the following symptoms: fall of arterial pressure, acceleration of respiration, and increased intestinal movements. All these symptoms are not produced in every case. The fall of arterial pressure due to anaphylactic shock from diglycylglycine should be greater than 10 cm., as a gradual fall to this amount can be produced by the first injection of this substance into an animal. The effect on blood coagulation cannot be employed as a criterion of anaphylactic action, as the polypeptide itself is not without action. S. B. S.

Fate of *N*-α-Aminohexoic Acid in the Phloridzinised Dog. ISIDOR GREENWALD (*J. Biol. Chem.*, 1916, **25**, 81—86).—The administration of the dextro- or of the lævo-rotatory stereoisomeride of *n*-α-aminohexoic acid to the phloridzinised dog is followed by the appearance in the urine of an amount of "extra" dextrose approximately equivalent to that of the amino-acid ingested. In some cases an increased excretion of acetone and of β-hydroxybutyric acid is also observed. H. W. B.

Formation of Specific Proteoclastic Ferments in Response to the Parenteral Injection of Foreign Proteins. FLORENCE HULTON (*J. Biol. Chem.*, 1916, **25**, 163—171).—The author has injected solutions of certain proteins parenterally into rabbits, and has afterwards tested the sera for the presence of enzymes capable of hydrolysing the specific protein injected. The criterion of hydrolysis adopted was the increase of non-protein nitrogen. Protamine,

phaseolin, gliadin, caseinogen, edestin, lactalbumin, Bence-Jones protein, and globulin from soja bean were the proteins injected and, in each case, not the slightest indication of the formation of a proteoclastic enzyme was obtained. H. W. B.

The Storing of Acid Dyes in the Animal Organism, a Physical Process. WILH. VON MOELLENDORFF (*Kolloid Zeitsch.*, 1916, **18**, 81—90).—Attention is drawn to the difference in the behaviour of acid and basic dyes towards living cells. The storing up of acid dyes in the organism is found to depend very largely on the dispersity of the dyes. The tendency to accumulate diminishes as the degree of dispersity increases. There is no evidence to show that acid dyes combine with the cell substance, although it is probable that such combination occurs in the case of basic dyes. The solubility of acid dyes in lipoid substances tends to diminish the accumulation of these in the cells. H. M. D.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Nitrogenous Matter on the Lactic Fermentation of Dextrose by the Bacillus Bulgaricus. LEOPOLDO LÓPEZ PÉREZ (*Anal. Fis. Quim.*, 1916, **14**, 165—193).—An exhaustive series of determinations of the amount of lactic acid produced by the fermentation of dextrose under varying conditions. Inter alia, the presence of nitrogenous matter is essential to the fermentation, and the process is much facilitated by the addition of calcium carbonate. A. J. W.

The Scission of Urea by Bacteria. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **74**, 109—115).—Bacteria obtained by U. Friedemann, which could produce tumours on plant bulbs, were found to be capable of decomposing urea. The bacteria were not active in the presence of antiseptics. The precipitates obtained from the bouillon cultures by extraction with sodium chloride or by shaking with kieselguhr were found to be active, but the author has not yet succeeded in isolating a urease from the bacteria. S. B. S.

The Action of Serum on the Scission of Urea by Bacteria, and the Problem of the Increase of Bacterial Virulence in the Animal Body. MARTIN JACOBY (*Biochem. Zeitsch*, 1916, **74**, 116—122).—Serum increases the action of the bacteria on urea. The auxo-substance in this case is not an amino-acid, for glycine inhibits the urease action. On heating the serum for twenty minutes at 70° its auxo-action is somewhat increased. On dialysis, the auxo-action is not lost, and there is some evidence from the

dialysis experiments that two auxo-substances are present. Furthermore, if the dried serum is treated with alcohol, both the part soluble and the part insoluble in this solvent are active, although the former is only present in small quantities. The author draws attention to the bearing of the facts discovered on the mechanism of the increase of virulence of bacteria when these pass through an animal body. S. B. S.

Some Factors that Influence Nitrate Formation in Acid Soils. E. B. FRED and E. J. GRAUL (*Soil Sci.*, 1916, **1**, 317—338).—Four representative types of Wisconsin soils were used: (1) a neutral silt loam, (2) an acid sand, (3) an acid silt loam, and (4) an acid peat. The last three required respectively 13,050 lbs., 20,420 lbs., and 5,985 lbs. of calcium carbonate per acre to neutralise the top six inches of soil. All four types were found to contain nitrifying organisms; when, however, they are inoculated into a culture medium, the two silt loams nitrified much more rapidly than the sand and peat.

In the soils themselves nitrification was very slow in the acid sand and peat, although the production of ammonia from casein in these soils is very rapid. In the silt loams nitrification was much more rapid. The form of nitrogen seems to play an important part, organic nitrogen being more readily nitrified in acid soils than ammonium sulphate, whilst in non-acid soils the reverse is observed. These results and the fact that the source of the nitrifying bacteria is immaterial indicate that acid soils are not provided with nitrifying organisms especially resistant to acidity.

When organic nitrogenous compounds are present, addition of calcium carbonate has a temporary stimulating effect on nitrification which is reversed later on, coincidently with a great increase in nitrate-assimilating bacteria.

The conclusion is drawn that, under laboratory conditions, the beneficial effects of calcium carbonate on plants are not due to the direct effect on nitrification, which takes place before the plants require large amounts of nitrates. The rapid accumulation of nitrates, due to liming, may, moreover, result in a loss of nitric nitrogen through leaching. N. H. J. M.

The Sources of the Nitrogen of Yeast. TH. BOKORNY (*Chem. Zeit.*, 1916, **40**, 366—368).—Whilst all sorts of simple nitrogen compounds are available as food material for many species of fungi, yeast is somewhat more discriminating. Nitrates are unaltered and unassimilated, and the simple amines, such as ethylamine, are also unfavourable, and the yeast becomes quickly smothered by growths of bacteria. As a protection against this the presence of a fermentable sugar is advantageous. As the result of a series of experiments with various nitrogenous compounds in culture media, the following increases in weight of the dried plant substance after completion of fermentation (two days) were observed: ammonium sulphate in presence of sucrose, 71·8%; ammonium sulphate in presence of dextrose, 113%; asparagine and sucrose,

103·7%; aspartic acid and sucrose, 61·3%; leucine and sucrose, 90·3%; tyrosine, 61·3%; glycine, 25·8%; somatose (flesh albumose), a decrease of 9·7%, indicating that albumoses cannot be absorbed until peptonised; peptone with sucrose, 177·4%; peptone alone, serving also as carbon nutriment, 152%. Carbamide under certain conditions can also act as a nitrogenous food for yeast. In conclusion, the author discusses the question of the technical protein synthesis by means of yeast. G. F. M.

Influence of Partial Deacidification and of Temperature on the Decomposition of the Acids of Wine. H. MÜLLER-THURGAU and A. OSTERWALDER (*Chem. Zentr.*, 1916, i, 378—380; from *Landw. Jahrb. Schweiz*, 1915, 391—399).—Five 1-litre quantities of self-expressed grape juice were partly deacidified by the addition of 0·6, 1·3, 2·0, 2·66, and 4 grams of calcium carbonate respectively, and after five hours were transferred to sterilised fermentation flasks and kept at 11° in order to prevent decomposition of the acids during the fermentation. When fermentation was complete the wine, filtered from the lees, was placed in 300 c.c. sterilised flasks filled to the neck, and maintained at 15°. The contents first became quite clear, and then again cloudy at the commencement of the acid decomposition, clarifying once again towards the end of that process. In the strongly deacidified wines this decomposition occurred within a month, but with the only slightly or not at all deacidified wines only after about two months. The duration of the process with the latter wines was also longer than with the former; it varied from ten to twenty days. Whilst the decrease in acidity during the alcoholic fermentation varied on account of the varying content of tartar owing to the different amounts of calcium carbonate that had been added, the fall in acidity during the second fermentation was in every case almost the same, 4·2—4·39%. This, together with the almost uniform volatile acid and lactic acid content, shows that in each case an equal quantity of malic acid had been decomposed, and that no lactic fermentation had occurred. In conformity with the authors' previous experience, the fermentation was exclusively due to *Bacterium gracile*. Tables are appended showing the complete composition of the wines in question. The influence of temperature on the acid fermentation was studied between 4·5° and 36°, for which purpose the grape juice after alcoholic fermentation was placed in Panum thermostats. Temperatures of 20—26° were most favourable for the fermentation, but temperatures as low as 13—17° were sufficient to complete the action in the course of several months. Under 10° was unfavourable, whilst at 34·5—36° no acid fermentation occurred. G. F. M.

Formation of Acetaldehyde in Wine during and after Fermentation. H. MÜLLER-THURGAU and A. OSTERWALDER (*Chem. Zentr.*, 1916, i, 380—381; from *Landw. Jahrb. Schweiz*, 1915, 408—420).—The authors have deduced from the results of previous experiments that acetaldehyde appears as an intermediate pro

duct in alcoholic fermentation, and are now able to confirm this deduction by combining the aldehyde with sulphur dioxide during the fermentation, thus protecting it from further action. Samples of sterilised grape-juice were fermented and small quantities of potassium metabisulphite added at varying intervals of time. After completion of fermentation the wine contained considerable quantities of combined sulphur dioxide, and the distillate obtained from it after being rendered alkaline with sodium carbonate gave the Lewin and Rimini reactions for acetaldehyde. Similar experiments were carried out with solutions of sucrose and of dextrose. Calculated on 100 grams of fermented sugar, the distillate from four wine samples contained 890, 350, 634, and 454 mg., from the sucrose solutions 434 and 879 mg., and from the dextrose solution 583 and 1180 mg. of acetaldehyde. These quantities naturally do not represent more than a fraction of the acetaldehyde produced, since free sulphur dioxide was only present during a small portion of the total time during which fermentation was going on, whilst acetaldehyde is being formed during the whole period as an essential intermediate product of the sugar degradation. In finished wines, acetaldehyde may be produced by the oxidation of the alcohol; it can be caused either by exposure to the air or by storing in partly filled vessels. Treatment with sulphur dioxide removes it. G. F. M.

Prevention of Alcoholic Fermentation in Fruit and Grape Juice by means of Sulphurous Acid. H. MÜLLER-THURGAU and A. OSTERWALDER (*Chem. Zentr.*, 1916, i, 381—382; from *Landw. Jahrb. Schweiz*, 1915, 421—432).—The amount of sulphur dioxide requisite to kill yeast and prevent alcoholic fermentation is not the same for all fruit juices. The results of a close investigation show that in certain juices a considerable portion of the added sulphurous acid is rendered inactive by combination with fruit aldehydes (compare preceding abstract), and, moreover, the efficacy of the sulphur dioxide remaining free is variable, depending on the number and type of yeast cells present and the chemical composition of the juice. A higher percentage of tartaric, malic, or tannic acid increases the activity of the free sulphurous acid. Thus the juice from over-ripe grapes with 197 and 168 mg. of free sulphur dioxide per litre commenced in some of the flasks to ferment, whilst three samples of juice from early red fruit containing only 106, 136, and 134 mg. per litre did not ferment. Similarly with pears, one juice containing 453 mg. of sulphur dioxide per litre fermented, whilst another with 82 mg. per litre did not. A favourable food medium for the yeast cells increases their powers of resistance. If the sulphurous acid present is insufficient to kill all the cells, the remaining ones will multiply again and cause fermentation; it is not necessary for all the acid present to be oxidised to sulphate before this can occur, nor for the sulphur dioxide to be combined with aldehyde produced by the oxidation of the alcohol, as suggested by Martinand (*Mém. soc. agric. France*, 1911, **15**, 15). On the other hand, the

yeast growth is possible even in the presence of considerable quantities of sulphur dioxide, but when fermentation is scarcely perceptible, aldehyde is formed, not as the result of oxidation, but in consequence of the degradation of sugar (see preceding abstract), and the free sulphur dioxide is then rapidly removed by combination. G. F. M.

The Antiseptic Action of Substances of the Chloroamine Group. H. D. DAKIN, J. B. COHEN, M. DUFRESNE, and J. KENYON (*Proc. Roy. Soc.*, 1916, [*B*], **89**, 232—251).—The germicidal action of a number of chloroamines was investigated, both in the presence and the absence of serum, and these were found to be valuable antiseptics. Almost all substances containing the NCl group have germicidal action; the presence of more than one such group does not appreciably increase the action; molecule for molecule, the action is greater than that of sodium hypochlorite; substitution in the aromatic nucleus by Cl, Br, I, CH_3, C_2H_5, or NO_2 groups does not increase germicidal action; the chloroamine derivatives of the sulphonchloroamide type of naphthalene and other bicyclic compounds closely resemble in their action the simpler aromatic chloroamines; the few bromoamines examined show a slightly lower germicidal action than the corresponding chloroamines, but are more active than sodium hypobromite; they react more readily with proteins than does sodium hypobromite. Derivatives of proteins containing the NCl group, prepared by the action of sodium hypochlorite, are also strongly germicidal.

The chief substances investigated were the sodium sulphonchloroamides, of which the *p*-toluene derivative, which can be readily and cheaply obtained, is very satisfactory, and is designated "chloramine T." The method of obtaining the sulphonchloroamides is indicated in the following equations:

$R\cdot SO_2\cdot NH_2 + 2HClO = R\cdot SO_2\cdot NCl_2 + 2H_2O$;

$R\cdot SO_2\cdot NCl_2 + 2NaOH = R\cdot SO_2Na\colon NCl + NaClO + H_2O$.

The sodium sulphonchloroamides are soluble, crystalline substances. A method is given for preparing them without the necessity of isolating the dichloroamine.

The germicidal action of the sodium sulphochloroamides of the following was investigated: of benzene, *o*-toluene, *p*-toluene, *p*-ethylbenzene, *p*-chlorobenzene, *p*-bromobenzene, *p*-iodobenzene, *m*-nitrobenzene, *o*-, *m*-, and *p*-xylene, *o*-dichlorobenzene, *o*-nitrotoluene, mesitylene, ψ-cumene, dibenzyl, α-naphthalene, β-naphthalene, and also sodium 1:4-naphthalenedisulphonchloroamide, sodium 2:6-naphthalenedisulphonchloroamide, sodium 2:7-naphthalenedisulphonchloroamide, sodium *o*-sulphochloroamidobenzoate, sodium *p*-diphenyldisulphonchloroamide, sodium diphenylmethanedisulphonchloroamide, and sodium dibenzyldisulphonchloroamide. The germicidal action also of the following chloroamines was investigated: quinonechloroimide, quinonedichloroimide, acetylchloroaminobenzene, *p*-chloroacetylchloroaminobenzene, 2 : 4-dichloroformylchloroaminobenzene, 2 : 4-dibromoacetylchloroaminebenzene, acetylchloroaminochloroxylene, diacetylchloroaminodi-

chlorobenzene, benzobromoamide, sodium benzenesulphonbromoamide, *p*-xylenesulphonbromoamide; the action was also investigated of chlorinated blood albumin, egg albumin, caseinogen, and peptones.

The method of germicidal action has not been definitely ascertained, but the chloroamines act on proteins and on amino-acids readily, and the reaction in the latter case may be represented by the following typical equations:

$$CH_3\cdot C_6H_4\cdot SO_2Na\colon NCl + NH_2\cdot CH_2\cdot CO_2H = NHCl\cdot CH_2\cdot CO_2Na + CH_3\cdot C_6H_4\cdot SO_2\cdot NH_2.$$

$$NHCl\cdot CH_2\cdot CO_2Na + H_2O = CH_2O + CO_2 + NaCl + NH_3.$$

An aldehyde is the usual product of the reaction.

Reference is also made to a crystalline compound of hexamethylenetetramine and calcium hypochlorite, which is prepared by adding strong bleaching powder solution to hexamethylenetetramine, and is precipitated in the form of fine crystals. Although this compound has strong germicidal properties, it readily decomposes on keeping, and is too unstable for practical use as an antiseptic. S. B. S.

Studies in Permeability. III. Absorption of Acids by Plant Tissue. MILDRED HIND (*Ann. Bot.*, 1916, **30**, 223—238).—The hydrogen ions of all the acids employed are rapidly absorbed by plant tissue from dilute solutions. With mineral acids the exosmosis of electrolytes produced is considerably less than in the case of formic and acetic acids.

Evidence was obtained which suggests that proteins may have an essential part in the absorption of acids. No indications were obtained that lecithin has any influence. N. H. J. M.

Formation of Acetaldehyde in Fruits. H. MÜLLER-THURGAU and A. OSTERWALDER (*Chem. Zentr.*, 1916, i, 380; from *Landw. Jahrb. Schweiz*, 1915, 400—407).—Attempts were made to determine the aldehyde content of pears, apples, and grapes at various stages of ripeness by adding excess of potassium metabisulphite to the freshly expressed juice, and then estimating the free and the total sulphur dioxide. The difference, namely, the combined sulphur dioxide, was regarded as an approximate measure of the aldehyde present. Alternatively, the juice was subjected to a preliminary distillation in a stream of carbon dioxide, and the distillate (250 c.c. from 2 litres), collected in a well-cooled receiver, was examined as above described, but the values found were always too low. The distillate, nevertheless, gave the Lewin and Rimini reactions for acetaldehyde. The results indicated that acetaldehyde is only present in notable quantity in pears, namely, from about 4 to 300 mg. per litre, according to increasing ripeness. In apple-juice 14—52 mg. per litre were found, but only 1—6 mg. in the distillate. No aldehyde could be detected in grape-juice, and in all cases with the commencement of fermentation the aldehyde rapidly disappears. G. F. M.

The Distribution of Maltase in Plants. I. The Function of Maltase in Starch Degradation and its Influence on the Amyloclastic Activity of Plant Materials. WILLIAM ALFRED DAVIS (*Biochem. J.*, 1916, **10**, 31—48).—Reasons are given for supposing that maltase is always present in plants where starch degradation occurs, and that the failure to detect it is due to the facts that it is endocellular in origin and readily destroyed at temperatures above 50°. It occurs in considerable quantities both in germinated and ungerminated cereals. As the result of the study of the rate of action on maltose and starch, the conclusion has been drawn that this enzyme acts only on maltose which has been derived from the starch by the action of the other amyloclastic ferments, and that no direct scission of dextrose from starch ever occurs. The action of the enzymes of germinated barley on starch is similar to that of the enzymes of taka-diastase, but the latter is richer in maltose-forming enzymes, so that the dextrin stage in starch degradation is passed through more rapidly. In both cases dextrose is formed from maltose by the action of maltase. S. B. S.

The Distribution of Maltase in Plants. II. The Presence of Maltase in Foliage Leaves. ARTHUR JOHN DAISH (*Biochem. J.*, 1916, **10**, 49—55).—The crushed pulp of the leaves examined (*Tropæolum*, potato, dahlia, turnip, sunflower, and mangold) acts on soluble or gelatinised starch to form reducing sugars, the greater part of which consists of dextrose. There is no doubt that these leaves, therefore, contain a maltase. When a relatively large excess of starch is used, the conversion is incomplete, and maltose is found amongst the degradation products. This is due to the fact that the action of the endocellular maltase is limited under the conditions of the experiment, having low solubility and low powers of diffusion. S. B. S.

The Distribution of Maltase in Plants. III. The Presence of Maltase in Germinated Barley. ARTHUR JOHN DAISH (*Biochem. J.*, 1916, **10**, 56—76).—The presence of maltase in germinated barley can be shown when the finely powdered grain is allowed to act on maltose and starch at 38°. In these circumstances dextrose and maltose can be formed from starch, the proportion of the former increasing as that of the latter diminishes. The dextrose is got by the action of maltase on maltose, and not by direct scission from starch. The action of the germinated barley is similar to that of taka-diastase. It has not been found possible to isolate a maltase from the material by extraction with water and precipitation of the extract thus obtained by alcohol; preparations obtained in this way act as ordinary malt extracts, and form only dextrin and maltose from starch. From numerous experiments on the auto-digestion of germinated barley and its action on added starch, the conclusion is drawn that the degradation of starch takes place in a series of stages: starch $\longrightarrow$ soluble starch $\longrightarrow$ dextrins $\longrightarrow$ maltose $\longrightarrow$ dextrose. The maltose was estimated in the

presence of dextrose by fermentation with pure cultures of yeast (*S. exiguus* and *S. marxianus*), which are free from maltase, by the method described by Davis and Daish. S. B. S.

Ceanothus velutinus (Snow Brush) as a Source of Wax and Tannin. CHAS. C. SCALIONE and HERBERT S. BLAKEMORE (*J. Ind. Eng. Chem.*, 1916, **8**, 411—413).—The leaves and twigs of *Ceanothus velutinus*, a common shrub growing in California, yield 7·3% of wax and 17·3% of tannins. The wax consists of free hydrocarbons and cerotic acid, together with ceryl and myricyl palmitates and stearates. A trace of glycerides appears to be present. The tannins are of the catecholic variety, and are suitable for tanning purposes. W. P. S.

The Presence of Cyclic Amino-acids in Ergot of Rye. SIGMUND FRÄNKEL and JOSEF RAINER (*Biochem. Zeitsch.*, 1916, **74**, 167—169).—The following acids have been found in ergot extracts: tyrosine, tryptophan, and histidine. Tryptophan was not found in all preparations investigated. S. B. S.

Peptolytic Enzyme of Ficus carica. N. T. DELEANU (*Bull. Sci. Acad. Roumaine*, 1916, **4**, 345—354).—The peptolytic enzyme of the latex of *Ficus carica* is found to be identical with that of *Carica papaia*. When left in contact with lead sulphide for a shorter or longer time, these enzymes suffer total or partial loss of their activity, and the latter is arrested completely by hydrogen sulphide. During the period of growth, the degradation of the proteins present in the leaves of *Ficus carica* yields only proteose, peptone, and amino-acids of the type of tyrosine; glutamine probably exists in the leaves, but not the alloxuric bases, histidine, arginine, choline, or betaine. During auto-digestion at high temperatures degradation products are formed which are precipitated by phosphotungstic acid. T. H. P.

Presence of Urease in Higher Plants. M. W. BEYERINCK (*Chem. Weekblad*, 1916, **13**, 443—444).—Mom's statement (this vol., i, 358, ii, 203) as to the absence of urease in soja beans is not confirmed by the author, who found a number of specimens to be rich in this substance. A. J. W.

Alkaloids of some Egyptian Solanaceæ. FRANK HUGHES (*Ministry of Agric., Egypt, Techn. Sci. Service*, Bull. 3, 1916. Compare Dunstan and Brown, T., 1899, **75**, 71; 1901, **79**, 72).—The Egyptian *Hyoscyamus muticus* may contain only 0·6% of alkaloid if collected after the ripening of the seed, and from 1·5—2% about the time of flowering. Great care is necessary in drying the material. A sample of expressed juice which was evaporated under reduced pressure was found to have lost the whole of the alkaloid by hydrolysis.

The method employed for extracting and purifying the alkaloid is described. N. H. J. M

Some Constituents of Sumbul Root. FREDERICK W. HEYL and MERRILL C. HART (*J. Amer. Chem. Soc.*, 1916, **38**, 432—446).—A systematic examination of the root of *Ferula Sumbul*, an official drug in the United States, imported from Moscow. The most conspicuous portion of the extract is a resin, soluble in alcohol but insoluble in water.

Percolation with cold alcohol removed about 20% of the material. Of this, the constituents soluble in water were sucrose, lævulose, a glucoside of umbelliferone, acetic acid, and betaine. The insoluble resin was further extracted with light petroleum, ether, chloroform, ethyl acetate, and alcohol. The petroleum extract contained a white, acid resin, which yielded vanillic acid on hydrolysis, and also a fat, a large proportion of which was unsaponifiable. Of this, one fraction, b. p. 168—173°/12 mm., corresponded with $C_8H_{13}O$, whilst a phytosterol, $C_{27}H_{46}O$, m. p. 134—135° (acetate, m. p. 121—122°), was also isolated. Acetic, butyric, valeric, tiglic, angelic, oleic, linoleic, cerotic, palmitic, and stearic acids were identified among the fatty acids. The ethereal extract contained a phytosterolin, $C_{33}H_{56}O_6$, m. p. 290° (acetate, m. p. 159—160°), a trace of vanillin, a neutral resin, which yielded umbelliferone on hydrolysis, and an acid resin, which gave vanillic acid and umbelliferone on hydrolysis. The chloroform extract consisted largely of a glucosidic resin, which yielded umbelliferone and dextrose on hydrolysis. The ethyl acetate extract was not glucosidic, but also gave umbelliferone on hydrolysis. The final alcoholic extract when submitted to acid hydrolysis yielded umbelliferone and a reducing sugar. J. C. W.

Action of some Organic Compounds on Plants. GIACOMO CIAMICIAN and CIRO RAVENNA (*Ann. Chim.*, 1915, [ix], **3**, 5—27. Compare A., 1908, ii, 773; 1909, ii, 604; 1910, ii, 234; 1911, ii, 643, 761).—*o*-, *m*-, and *p*-Cresols in the form of their calcium salts, potassium phenolsulphonate, catechol, and quinol were injected into a number of tobacco plants and after six to eight weeks the plants were collected and their alkaloid content determined and compared with that of control plants. The differences obtained were too slight to allow of any conclusions being drawn. Similar experiments were conducted with nicotine in the form of its hydrogen tartrate, the results indicating that the nicotine injected was partly destroyed by the plants, but to a lesser extent than the other substances previously studied.

Tobacco seeds in a state of rest, similar seeds germinated in the absence of nitrogenous compounds, and tobacco plants in various stages of growth were examined for the presence of *iso*amylamine. This base could not be detected in resting seeds, but was probably present in the germinating seeds. It was absent from young plants, but present in more developed plants, the latter also showing an increase in nicotine. There is no indication of any genetic relationship between *iso*amylamine and nicotine in the tobacco plant.

A large amount (730 grams) of alkaloid hydrochlorides accumulated from tobacco plants during a number of years was carefully

examined for the presence of pyrrole bases, but, contrary to the results of Pictet and Court (A., 1907, i, 954), none could be found. In addition to *iso*amylamine and nicotine, trimethylamine was isolated in the form of its hydrochloride.

Maize plants were inoculated with gallic acid in the form of its potassium salt, and after five weeks the plants were harvested and examined, but they showed no sign of special formation of glucosides or of substances similar to tannin, although the gallic acid had almost entirely disappeared.

Maize and sorghum plants were similarly inoculated with acetone in the form of its bisulphite compound in the presence of an equal weight of dipotassium hydrogen phosphate. The leaves were gathered and examined, but showed no sign of formation of glucosides hydrolysable by emulsin, but the acetone was eliminated by the plants by an oxidation process. W. G.

Cyanogenesis in Plants. Tridens flavus (Tall Red Top). ARNO VIEHOEVER, CARL O. JOHNS, and CARL L. ALSBERG (*J. Biol. Chem.*, 1916, **25**, 141—150).—*Tridens flavus*, a common grass, contains a considerable amount of hydrogen cyanide. The maximum quantity occurs in the inflorescence tops (0·0037%), whilst the root contains only a trace. Hydrogen cyanide is not present in the ripe seeds.

Specimens of the grass collected in August contain larger quantities of hydrogen cyanide than those collected in September. By October all traces of hydrogen cyanide have disappeared from the plants, but they still contain an enzyme capable of liberating hydrogen cyanide from amygdalin. H. W. B.

Sulphofication. P. E. BROWN and H. W. JOHNSON (*Soil Sci.*, 1916, **1**, 339—362).—Pot experiments are described in which oats were grown in a loam rich in organic matter, and containing 911 lbs. of phosphorus and 2487 lbs. of sulphur per acre (2,000,000 lbs. of surface soil). It was found that calcium sulphate, monocalcium phosphate, acid phosphate, and rock phosphate all increased the sulphofying and ammonifying powers of the soil, although the results were not always parallel. Phosphates increase the yield of oats, whilst sulphates had no effect on the yields.

Sulphofication is not injuriously affected by ordinary applications of calcium sulphate, and is increased by calcium carbonate even when applied in excessive amounts; small amounts of magnesium carbonate are favourable, whilst large amounts depress sulphofication below that in the same soil with its acidity unneutralised.

N. H. J. M.

Constituents of the Maize Embryo. E. WINTERSTEIN and F. WÜNSCHE (*Zeitsch. physiol. Chem.*, 1916, **95**, 310—336).—The composition of the maize embryo differs considerably from that of the wheat grain. It does not contain free arginine, and only a trace of glutamine. The remainder of the comparatively small proportion of non-protein nitrogenous compounds consists of two

bases—guanidine, which is not present in the wheat embryo, and a *compound*, $C_{17}H_{37}O_{8\cdot5}N_6$, which could not be obtained in crystalline form.

The proteins of the maize embryo consist chiefly of albumins with a small proportion of globulin. A nucleic acid, such as occurs in the wheat embryo, is not present.

The maize embryo contains about four times as much fat as the wheat embryo. Sitosterol and phosphatides are present, as well as the glycerides of higher and lower fatty acids.

The carbohydrates of the maize embryo comprise a pentoside and a considerable quantity of inositol phosphoric acid. H. W. B.

The Zymase and Carboxylase of Potato and Sugar-beet. J. Bodnár (*Biochem. Zeitsch.*, 1916, **73**, 193—210).—Both zymase and carboxylase can be isolated from the reserve depôts of potato and sugar-beet, in confirmation of the observations of Stoklasa. The fermentative actions are not due to bacteria, for when these have been isolated from the fermentation mixtures they do not produce alcoholic fermentation of dextrose. No alcohol is produced by the enzyme preparations made from potatoes with ring disease, but a large amount of acetic acid is formed. This is produced by an alcohol oxydase of the soil bacteria, which obtain entrance into the crude enzyme preparation from the diseased tubers. The enzyme preparation from beets suffering from beet-rot produces only small amounts of alcohol and carbon dioxide, but the reason for this is unknown. In addition to zymase, carboxylase can also be isolated from beet and potato, and it is possible to obtain preparations in which only the carboxylase action exists. The differences in stability, etc., between the two enzymes are similar to those discovered by Neuberg in his investigations on the zymase and carboxylase of yeast. S. B. S.

The Dependence of the Resorption of the Potassium Ion on the Presence of the Sodium Ion in the Organism of the Sugar-beet. Julius Stoklasa (*Biochem. Zeitsch.*, 1916, **73**, 260—312).—The chlorides of potassium and sodium when added singly in solution to a soil of mixed sand and peat cause an increase in both the bulk of a sugar-beet plant and of the sugar content as compared with plants grown in a similar way but receiving the same amount of water without salts. The increase in mass and sugar caused by $N/10$-potassium chloride is markedly more than that caused by $N/10$-sodium chloride. Concentrations of more than $2N/10$-sodium chloride act deleteriously on the plant, and the growth is less than with the lower ($N/10$) concentrations. The plants can, however, tolerate a higher concentration of the potassium salt; $3N/10$-potassium chloride causes a depression in the amount of dry substance in the plant, but has no harmful influence on the amount of sugar in the beet. The best results in the plant growth are produced by a mixture of the two salts (each in $N/10$-concentration), and the toxic action of $3N/10$-potassium salt can be antagonised by the addition of $2N/10$-sodium salt.

Addition of calcium carbonate improves the action of a mixture of sodium and potassium chlorides, and antagonises the deleterious action of either salt when added in excess. Calcium chloride exerts a somewhat similar action, especially as regards the sugar content of the plant. The best results as regards sugar production are obtained by the use of a mixture of the chlorides of sodium, potassium, and calcium. Details are given by the author as to the influence of the salts on the beet plant in various stages of the growth. From anatomical examination at different stages of growth of plants treated in various manners, the conclusions are drawn that the potassium ion plays a considerable part in improving the turgescence, the chlorophyll production, and consequently the assimilation processes; the sodium ion appears to influence chiefly the growth of the cell-walls of the epidermis.

The resorption of potassium and sodium by the plants was also investigated. This reaches its maximum when both salts are employed together, each in the concentration $N/10$. The relationships between the relative amounts of potassium and sodium adsorbed under various conditions were also determined.

S. B. S.

Occurrence of Indole and Scatole. EDMUND O. VON LIPPMANN (*Ber.*, 1916, **49**, 106—107).—In the recovery of sugar by the strontia or baryta process, it is observable that if the molasses is boiled for some time with a considerable excess of the alkaline earth the vapours possess an unpleasant fæcal odour. Careful examination of the condensed vapours has revealed the presence of indole and scatole, the formation of these substances being probably due to the decomposition of protein substances or degradation products of these.

Mention is also made of the fact that the author in an examination of the sap of the pale shoots of beets which have sprouted when stored has observed the presence of substances which he believes to be *l*-tryptophan, *l*-phenylalanine, and hypaphorine (van Romburgh, A., 1911, i, 668). D. F. T.

Indole in Cheese. V. E. NELSON (*J. Biol. Chem.*, 1916, **24**, 533—536).—Indole is present in limburger and camembert cheeses and in "Handkäse." Limburger cheese also contains phenol. Cheddar, Swiss, "Gammalost," brick, and roquefort cheeses do not contain indole or phenol. Scatole is absent in all cases.

The amount of indole in limburger cheese increases during the ripening process until it reaches as much as 1 part in 52,800 parts of cheese.

The organism responsible for the production of the indole in cheese has not been ascertained, but lactic and bulgaricus forms of organisms when grown on media containing tryptophan did not produce indole or scatole. H. W. B.

Organic Chemistry.

Process of Treating Hydroxy-compounds with Acetylene and New Industrial Products [Diolefines] Arising therefrom. G. BOITEAU (Fr. Pat., 477560; from *J. Soc. Chem. Ind.*, 1916, **35**, 617).—The action of acetylene on hydroxy-compounds, particularly alcohols, by heating in presence of a mercury catalyst, produces ethers which, on dehydration by heating with various oxides, silicates, sulphates, or phosphates, are converted into substances of industrial importance. Thus from primary and secondary alcohols diolefines are obtained; methyl alcohol and acetylene, for example, give an ether, $C_4H_{10}O_2$, which on dehydration loses 2 mols. of water with the formation of butadiene. G. F. M.

Saponification of Chlorine Derivatives of Aliphatic Hydrocarbons. (Preparation of Methyl Alcohol.) E. SZARVASY (U.S. Pat., 1181697; from *J. Soc. Chem. Ind.*, 1916, **35**, 707).—Aliphatic chlorohydrocarbons, such as methyl chloride, are hydrolysed by heating them (for example, at 140°) under pressure (for example, 20—24 atm.) with an alkaline solution, the vessel being rotated so as to cover its interior with a film of the reacting liquids. G. F. M.

Preparation of Ethylene Dibromide. E. B. R. PRIDEAUX (*Chem. News*, 1916, **113**, 277).—An arrangement of apparatus is indicated, whereby large quantities of ethylene dibromide can be prepared, in such a way that the ethylene is completely converted into dibromide free from bromine, in one operation and with the least loss of bromine. The working is on the counter-current principle, and is continuous. The ethylene is prepared by passing alcohol vapour through heated phosphoric acid. T. S. PA.

Preparation of γ-Methylbutinol, its Homologues and Analogues. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P., 291185; from *J. Soc. Chem. Ind.*, 1916, **35**, 707—708).—A mixture of γ-methylbutinol or its homologues or analogues with ethyl alcohol is obtained by the action of acetylene on acetone or its homologues or analogues in presence of alkali ethoxide. On shaking with concentrated sodium hydroxide and cooling with ice the alcoholate of γ-methylbutinol separates in crystals; it is redissolved in water, and the cold solution saturated with carbon dioxide and extracted with ether. From the ethereal extract the methylbutinol is recovered by distillation. G. F. M.

Neutralisation of the Affinity of Main and Subsidiary Valencies in Compounds of a Higher Order. II. J. V. DUBSKY (with TH. BEER and H. FRANK) (*J. pr. Chem.*, 1916, [ii], **93**, 142—161. Compare A., 1914, ii ,732).—The ability of metallic

xanthates to form additive compounds with pyridine and ammonia has been further investigated, and the aluminium salts of sulphonic acids have been prepared.

Cuprous methyl xanthate (Ragg, A., 1910, i, 154) dissolves in pyridine to form the *compound*, $CuCS_2\cdot OMe,C_5H_5N$, which separates as a canary-yellow powder. *Nickel methyl xanthate*,

$$Ni(S\cdot CS\cdot OMe)_2,$$

obtained by mixing solutions of nickel sulphate and potassium methyl xanthate, crystallises from ethyl acetate in large, black needles, decomp. 158—160°, and forms *compounds* with 2, 3, and 4 molecules of pyridine. *Zinc methyl xanthate* separates from benzene in large, white granules, and forms a yellow *compound* with 2 molecules of pyridine. *Mercuric methyl xanthate* crystallises unchanged from pyridine in pearly scales, m. p. 135—137° (decomp.). *Ferric methyl xanthate* forms large, black crystals, and the *compound*, $Fe(CS_2\cdot OMe)_3,3C_5H_5N$, crystallises in golden-yellow leaflets, m. p. 88—90°. *Cobaltic methyl xanthate*, $Co(CS_2\cdot OMe)_3$, forms glistening, black, rhombic crystals, but does not combine with pyridine. *Chromic methyl xanthate*, $Cr(CS_2\cdot OMe)_3$, forms large, black crystals, m. p. 150—152° (decomp.). *Bismuth methyl xanthate* crystallises in long, deep yellow needles, and slowly decomposes in pyridine solution. *Lead methyl xanthate* forms slender, pale yellow needles.

Cuprous ethyl xanthate forms the canary-yellow *compound*, $CuCS_2\cdot OEt,C_5H_5N$, decomp. 120—126°. *Nickel ethyl xanthate*, m. p. 137°, forms a *compound* with $2C_5H_5N$, m. p. 124° (decomp.). Barium ethyl xanthate and *bismuth ethyl xanthate*, yellow, quadratic tablets, m. p. 106°, do not combine with pyridine, but zinc ethyl xanthate forms the *compound*, $Zn(CS_2\cdot OEt)_2,2C_5H_5N$, yellow prisms and needles.

Nickel methyl and ethyl xanthates form pale blue, labile *compounds* with $6NH_3$. Zinc methyl and ethyl xanthates form well-crystallised *compounds* with $2—3NH_3$.

The following *aluminium* salts of the general formula

$$Al(OH_2)_6,3SO_3R,3H_2O,$$

were obtained by double decomposition of aluminium sulphate and the barium sulphonates: *benzenesulphonate*, very hygroscopic; *toluene-ω-sulphonate*, snow-white needles; p-*phenolsulphonate*, thick tablets; *α-naphthalenesulphonate*, crystalline powder; *β-naphthalenesulphonate*, glistening leaflets. J. C. W.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. II. PRAFULLA CHANDRA RÂY (T., 1916, **109**, 603—612. Compare A., 1916, i, 246).—An extension of the earlier investigation of the interaction of mercury mercaptide nitrites and the alkyl iodides. The product obtained from mercury methylmercaptide nitrite and butyl iodide was found to have the composition $MeS_2\cdot C_4H_9,HgI_2,C_4H_9I$, instead of the expected Me_2S_2,HgI_2,C_4H_9I, and further examination showed that the methyl radicle can be displaced by its other homologues, the effect apparently being dependent, in part at least, on mass action. It is noteworthy that

in the separated compound, Me_2S_2,HgI_2,MeI, the methyl radicle is not displaceable by a higher homologue, the displacement occurring only when this substance is in a nascent condition.

Although according to the formulation annexed, the iodine atoms attached to sulphur might be expected to exhibit different behaviour from that in the complex group HgI, no distinction is perceptible with an acetone solution of silver nitrate, which quantitatively removes the whole of the iodine, and, indeed, provides a very convenient means for the estimation of the iodine in these compounds, as well as for the conversion of the disulphonium alkyl mercuri-iodide into the corresponding nitrate.

$$\begin{array}{ccc} \mathrm{R} & & \mathrm{HgI} \\ \mathrm{R{-}\dot{S}} & \mathrm{-} & \mathrm{\dot{S}{-}R'} \\ \dot{\mathrm{I}} & & \dot{\mathrm{I}} \end{array}$$

The compounds described below were prepared by the method already described; except where otherwise stated, they were of a pale yellow colour resembling flowers of sulphur. Mercury methylmercaptide nitrite and methyl iodide yielded the *substance* Me_2S_2,HgI_2,MeI, m. p. 162°; with ethyl iodide the mercury methylmercaptide nitrite gave the *substance* $MeEtS_2,HgI_2,EtI$, m. p. 67°; with *n*-propyl iodide, *n*-butyl iodide, and *iso*amyl iodide respectively the products were the *substances*

$$MePr^{\alpha}S_2,HgI_2,Pr^{\alpha}I;\ MeS_2{\cdot}C_4H_9,HgI_2,C_4H_9I,$$

m. p. 108°, and $MeS_2{\cdot}C_5H_{11},HgI_2,C_5H_{11}$, a semi-solid, yellowish-green mass.

The general nature of this class of reaction is demonstrated by the conversion of 2-mercaptothiazoline into the corresponding *mercury 2-mercaptothiazoline nitrite*, $\begin{array}{l}CH_2{-}S\\|\\CH_2{\cdot}N\end{array}\!\!>C{\cdot}S{\cdot}HgNO_2$, by treatment in alcoholic solution with mercuric nitrite, the product being able to react with ethyl iodide with formation of the expected disulphonium *compound*, $\left(\begin{array}{l}CH_2{-}S\\|\\CH_2{\cdot}N\end{array}\!\!>CS\right)_2,HgI_2,EtI$, a yellowish-brown solid. The interaction of dithiolethylene and mercuric nitrite produced a white, crystalline mixture of two *mercury ethylenemercaptide nitrites*, $HgNO_2{\cdot}S{\cdot}C_2H_4{\cdot}S{\cdot}HgNO_2$ and

$$HgNO_2{\cdot}S{\cdot}C_2H_4{\cdot}S_2{\cdot}C_2H_4{\cdot}S{\cdot}HgNO_2,$$

both of which react with ethyl iodide, yielding a disulphonium *compound* of the formula $C_2H_4{<}\begin{array}{l}S_2\\S_2\end{array}{>}C_2H_4,HgI_2,EtI$.

Mercury ethylmercaptide nitrite and *n*-propyl iodide reacted with formation of the *substance* $EtPr^{\alpha}S_2,HgI_2,Pr^{\alpha}I$, m. p. 77°, the production of $Et_2S_2,HgI_2,Pr^{\alpha}I$ as described in the earlier publication probably being due to the use of a smaller proportion of propyl iodide, with the result that no displacement of the ethyl group occurred. With mercury ethylmercaptide nitrite and *n*-butyl iodide the *substance* $EtS_2{\cdot}C_4H_9,HgI_2,C_4H_9I$ was obtained as a dark, treacly liquid, the *substance* $EtS_2{\cdot}C_5H_{11},HgI_2,C_5H_{11}I$, produced by the action of *iso*amyl iodide, being of similar consistency. The *substance* $MeEtS_2,HgI_2,MeI$, formed by the interaction of mercury ethylmercaptide nitrite and methyl iodide, was a pale yellow, crystalline solid, m. p. 84—85°.

The *substances* $MePr^{a}S_2,Hg(NO_3)_2,Pr^{a}NO_3,C_3H_6O$ and
$$Et_2S_2,Hg(NO_3)_2,Pr^{a}NO_3,C_3H_6O,$$
were viscid liquids obtained by the double decomposition of silver nitrate with the corresponding iodides in acetone solution; each product retains a molecule of acetone in combination.

When ethyl disulphide and mercuric iodide in molecular proportions are heated with excess of ethyl iodide for three hours, the *substance* Et_2S_2,HgI_2,EtI, yellow crystals, m. p. 110°, indistinguishable from the product of interaction of mercury ethylmercaptide and ethyl iodide, is obtained; this result appears to render doubtful the formula Et_2S,HgI_2,EtI, given by Hilditch and Smiles (T., 1907, **91**, 1397) to a compound, m. p. 110°, obtained by the interaction of ethyl disulphide and mercuric iodide in acetone solution.

D. F. T.

Preparation of Ethyl Acetate from Acetaldehyde. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (Eng. Pat., **1915**, 4887; from *J. Soc. Chem. Ind.*, 1916, **35**, 653).—Instead of increasing the catalytic activity of aluminium ethoxide by treatment with substances containing a halogen, by melting with aluminium hydroxide, etc. (see Eng. Pats., 1913, 26825, 26826; A., 1915, i, 3, 72), the same result may be attained by dissolving the molten ethoxide in anhydrous potassium alum, copper sulphate, or camphor, or by rapidly cooling the molten substance by pouring it on to a cold metal plate, or into a solvent. When, for example, 160 grams of the molten ethoxide (16·9% Al) are poured into 300 grams of boiling ethyl acetate, and to the solution 2665 grams of acetaldehyde are added rapidly with stirring, a product is obtained after several hours which on distillation gives a 90% yield of ethyl acetate.

G. F. M.

The Δ^{ζ} and Δ^{δ} Isomerides of Stearolic Acid. S. POSTERNAK (*Compt. rend.*, 1916, **162**, 944—946. Compare A., 1910, i, 459).—The remaining two of the six possible isomeric stearolic acids have now been prepared.

Δ^{ϵ}-Stearolic (tariric) acid (1 mol.) was melted and a current of dry hydrogen iodide led over it until it had absorbed two molecules. The resulting oil was boiled on a water-bath for three hours with 30% alcoholic potassium hydroxide, the potassium iodide was filtered off, the alcohol distilled off, the soaps dissolved in boiling water, and decomposed with dilute sulphuric acid. The crystalline product, obtained on cooling the liquid, consisted of a mixture of Δ^{ζ}, Δ^{ϵ}, and Δ^{δ}-stearolic acids, the first-named being removed by a single crystallisation from alcohol. The other two acids were converted into their di-iodo-derivatives in acetic acid solution, and these were separated by crystallisation from alcohol, the first product being *ζη-di-iodoelaidic acid*, nacreous plates, m. p. 68·25°. This, when treated with sodium in absolute alcohol, yielded *Δ^{ζ}-stearolic acid*, m. p. 49·25°. When oxidised with fuming nitric acid, this acid yielded pimelic acid and *ζη-diketostearic acid*, yellow, micaceous plates, m. p. 86·5°. The stearolic acid, on the addition

of 1 molecule of hydrogen iodide and subsequent reduction by zinc in acetic acid, gave Δ^{ζ}-*elaidic acid*, thin, oblong plates, m. p. 45·5°. cis-$\zeta\eta$-*Dihydroxystearic acid*, needles, m. p. 96·5°, was also prepared.

After the removal of $\zeta\eta$-di-iodoelaidic acid from the above mixture of di-iodo-derivatives, the iodine was removed from the residue, which was then submitted to fractional crystallisation through its sodium salt, the final product being Δ^{δ}-*stearolic acid*, nacreous plates, m. p. 52·5°. On oxidation with fuming nitric acid it yielded tridecoic acid, and $\delta\epsilon$-*diketostearic acid*, m. p. 94°. In addition, the following derivatives were prepared: $\delta\epsilon$-*di-iodoelaidic acid*, long, slender needles, m. p. 52°; Δ^{δ}-*elaidic acid*, rhombic plates, m. p. 47·5°; and $\delta\epsilon$-*dihydroxystearic acid*, needles, m. p. 94°.

W. G.

Glutaconic Acid. II. P. E. VERKADE (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1527—1539. Compare this vol., i, 249).—Some of the evidence promised in the earlier paper, to the effect that ordinary glutaconic acid is neither of the possible *cis*- nor *trans*-isomerides, but that the symmetrical formula proposed by Thorpe is most plausible, is now assembled.

Conductivity measurements give the values $K \times 10^6 = 171$, 176, and 164, at 0°, 25°, and 45° respectively; these values are about 3·7 times as great as those of glutaric acid, and indicate that no isomerisation occurs on heating.

Under the influence of various chemical and photo-chemical aids to *cis-trans*-isomerisation, glutaconic acid was unaffected.

The stable glutaconic acid gave a white precipitate with mercuric acetate of a compound which contained mercury exclusively in complex union, which is characteristic of *cis*-acids (Biilmann, A., 1902, i, 665; 1910, i, 347). The *compound* probably has the *formula* $\begin{array}{l}\mathrm{CO\cdot CH\cdot CH(OH)\cdot CH\cdot CO,3H_2O,}\\ \mathrm{O{-}Hg \qquad\qquad\quad Hg{-}O}\end{array}$ and its formation is explained by assuming that the labile *cis*-glutaconic acid is produced intermediately, and that one of the H-atoms of the methylene group is replaced by mercury.

Glutaconic acid was also found to absorb bromine vapour very rapidly, like *cis*-acids. Here, again, it is assumed that the labile *cis*-form is first produced from the normal acid. J. C. W.

Formaldehyde Containing Copper. HERMANN KUNZ-KRAUSE (*Chem. Zentr.*, 1916, i, 554; from *Apoth. Zeit.*, 1916, **31**, 66—67).—The presence of copper in formaldehyde is attributable to the volatility of copper formate, and also possibly to the formation of copper carbonyl, CuCO, both of which substances are derived from the copper spiral employed as a catalyst. Small quantities of copper can be detected to a certain limit by the blue colour produced on the addition of excess of ammonia to the formaldehyde solution. A more sensitive reaction is given by the addition of a few drops of pyridine when a greenish-blue colour is produced. A second and very sensitive test consists in the spontaneous volatilisa-

tion of the formaldehyde in the air, when, in presence of the least trace of copper, a bright greenish-blue colour is imparted, especially to the edges of the otherwise colourless metaformaldehyde remaining behind. The adsorptive action of cellulose may also be employed to detect small traces of copper in formaldehyde. Filtration of copper-free formaldehyde solution leaves the filter colourless, but in presence of the least traces of the metal a greenish-blue colour is imparted to the paper, which is particularly evident after drying and when viewed by transmitted light. Since the action of the cellulose is almost quantitative, simple filtration furnishes a convenient method for the removal of the copper. If filtration is not sufficient, a preliminary shaking of the liquid with filter paper or cellulose is recommended. Finally, the copper may be removed by electrolytic deposition on a fragment of iron, any acidity being previously neutralised by shaking with calcium carbonate and filtering prior to the introduction of the iron. The resulting formaldehyde solution is coloured brown by colloidal ferric hydroxide; after keeping for a few days this may be filtered off. G. F. M.

Preparation of Aldehyde-ammonia. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 290808; from *J. Soc. Chem. Ind.*, 1916, **35**, 617).—Aqueous solutions of aldehyde–ammonia are obtained by mixing excess of ammonia with acetaldehyde at low temperatures. The compound is used as an accelerator in the vulcanisation of natural and synthetic caoutchouc. G. F. M.

A Fourth Crystalline Penta-acetate of Galactose and some Related Compounds. C. S. HUDSON and J. M. JOHNSON (*J. Amer. Chem. Soc.*, 1916, **38**, 1223—1228).—Hudson and Parker (A., 1915, i, 652) have shown that when galactose penta-acetate, m. p. 142°, is boiled with acetic anhydride and a trace of zinc chloride, a second penta-acetate, m. p. 95·5°, is produced. Hudson (A., 1915, i, 651) found a third penta-acetate, m. p. 98°, in the mother liquor from the first penta-acetate, and this has now been transformed into a fourth penta-acetate by the action of acetic anhydride in presence of a little zinc chloride.

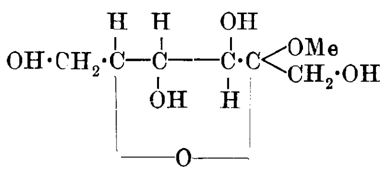
The fourth *galactose penta-acetate*, m. p. 87°, $[\alpha]_D^{20}$ in chloroform $+61°$, forms colourless, transparent prisms; it is only obtained in a small yield (about 10%), since in the equilibrium mixture of the third and fourth penta-acetates the third predominates. On heating the fourth penta-acetate with acetic anhydride and zinc chloride, it is largely reconverted into the third isomeride. Considerations are advanced which indicate that the first and second penta-acetates may be regarded respectively as β- and α-forms of penta-acetyl-γ-*cyclo*galactose, and the third and fourth as β- and α-forms of penta-acetyl-(α-, β-, δ-, or η-)*cyclo*galactose.

When a solution of the third galactose penta-acetate in chloroform is boiled with aluminium chloride and phosphorus pentachloride, a second crystalline *acetylchlorogalactose*, m. p. 67° (corr.), $[\alpha]_D^{20}$ in chloroform $-79·1°$, is obtained. The acetylchlorogalactose described by Skraup and Kremann (A., 1901, i, 507) has $[\alpha]_D$ in

chloroform $+213°$, and it therefore appears that the new isomeride has the same ring structure as exists in the third and fourth penta-acetates.

When the third penta-acetate is dissolved in acetic anhydride and treated at 0° with a saturated solution of hydrogen bromide in acetic acid, it is converted into a syrupy bromoacetyl derivative which, when dissolved in methyl alcohol and shaken with freshly prepared silver carbonate, yields a third crystalline *galactose tetra-acetate*, m. p. 71—73° (corr.), $[\alpha]_D^{20}$ in chloroform $-17{\cdot}8°$, and in water $-12{\cdot}9°$. This new tetra-acetate reduces Fehling's solution readily, and on acetylation is reconverted into the third penta-acetate; it shows muta-rotation with increasing dextro-rotation, and is therefore to be regarded as the β-form; its *phenylhydrazone* has m. p. 95° and $[\alpha]_D$ in chloroform $+15{\cdot}5°$. E. G.

Crystalline β-Methyl-lævuloside and its Tetra-acetate. C. S HUDSON and D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1916, **38**, 1216—1223).—When lævulose tetra-acetate is treated with methyl iodide and silver oxide in accordance with Purdie's method, a nearly quantitative yield of *β-methyl-laevuloside tetra-acetate*, m. p. 75—76°, is obtained, which crystallises in prismatic needles, has a bitter taste, and $[\alpha]_D^{20}$ in chloroform $-124{\cdot}6°$. On hydrolysing this compound with barium hydroxide, *β-methyl-laevuloside*, m. p. 119—120°, $[\alpha]_D^{20}$ in water $-172{\cdot}1°$, is produced, which forms large, thin plates, has a sweet taste, and can be sublimed in a vacuum. The substance does not reduce Fehling's solution until after hydrolysis by acid, and is thus distinguished from Irvine and Hynd's methyl-lævulose (T., 1909, **95**, 1224); it is not hydrolysed by yeast or emulsin, and does not exhibit muta-rotation. On the assumption that β-methyl-lævuloside is a γ-cyclo-derivative, its constitution is represented by the formula:



E. G.

Has Light an Influence on the Process whereby Bread becomes Stale? J. R. KATZ (*Zeitsch. physiol. Chem.*, 1915, **96**, 288—291).—An accelerating or inhibiting action of light on the process whereby bread becomes stale is not apparent. H. W. B.

Remarkable Property of Aldehydes of Preventing Bread from becoming Stale. J. R. KATZ (*Zeitsch. physiol. Chem.*, 1915, **96**, 314—322. Compare this vol., i, 465, 466).—The author has shown that when bread becomes stale its power of absorbing water and its content of soluble polysaccharides are both diminished (*loc. cit.*). If, however, the bread-crumb be suspended in a closed vessel containing a small quantity of any aldehyde, the bread

remains soft, and its water-absorptive capacity and content of soluble polysaccharides do not alter within forty-eight hours. Ketones and other volatile substances do not prevent the bread from becoming stale. H. W. B.

Separation of Aminoethyl Alcohol from the Hydrolysates of Phosphatides. H. THIERFELDER and OTTO SCHULZE (*Zeitsch. physiol. Chem.*, 1915, **96**, 296—308).—The phosphatide is hydrolysed with sulphuric acid in the usual way, and, after removal of the acid, the amino-bases are precipitated by basic lead acetate. The lead is removed as sulphide, and the bases converted into the chlorides, which are then purified by alcohol and animal charcoal. The concentrated solution of the chlorides is now mixed with calcium oxide, which liberates the free bases and simultaneously absorbs the water. The solid mass is extracted with ether in a Soxhlet apparatus, into the flask of which is placed an ethereal picrolonic acid solution. When the extraction is complete, the precipitated picrolonate of amino-ethyl alcohol is collected, washed with ether containing 12% of alcohol, dried, and weighed.

Choline is subsequently obtained from the residue in the thimble by extraction with alcohol. H. W. B.

Preparation of a Crystalline, Non-hygroscopic Salt of Choline. VEREINIGTE CHEMISCHE WERKE AKTIENGESELLSCHAFT (D.R.-P., 290740; from *J. Soc. Chem. Ind.*, 1916, **35**, 654).—By the action of 3 mols. of boric acid on 1 mol. of choline, a non-hygroscopic salt of choline, which crystallises well from water, is obtained. Its aqueous solutions do not suffer decomposition on boiling.
G. F. M.

Preparation of Therapeutic Compounds (Choral*iso*valeramide, and Butylchloral*iso*valeramide). J. LONGMAN (Eng. Pat., 1915, 5113; from *J. Soc. Chem. Ind.*, 1916, **35**, 617).—Chloral*iso*valeramide is obtained by heating chloral hydrate and *iso*valeramide at 90—95° for one hour, and crystallising the solidified product from benzene. It melts at 135—136°. The corresponding butylchloral compound is obtained in a similar way, heating in this case at 105—113° for ninety minutes. It melts at 126—127°. Both compounds have sedative, but not hypnotic, properties. G. F. M.

Influence of Varying Quantities of Water on the Decomposition of Nitrolime and the Formation of Dicyanodiamide. G. HAGER and J. KERN (*Zeitsch. angew. Chem.*, 1916, **29**, i, 221—223).—Five 100-gram quantities of nitrolime, containing 16·75% cyanamide nitrogen and 0·05% dicyanodiamide nitrogen, were treated with 5, 10, 15, 25, and 50 grams of water respectively, and kept in hermetically sealed bottles for periods extending up to seven months. At the end of this period the dicyanodiamide nitrogen amounted to 0·61%, 0·87%, 1·13%, 2·58%, and 9·17% respectively for the five samples. The addition of 15 grams of water had produced, therefore, a notable increase in dicyanodiamide nitrogen, and with larger quantities the conversion

approached the quantitative. It is therefore concluded that nitro-lime which has been allowed to get damp is unsafe for any other than immediate use, and that the use of water in the manufacture of a granular product is inadmissible. G. F. M.

The Action of Water on Cupric Thiocyanate. JAMES CHARLES PHILIP and ARTHUR BRAMLEY (T., 1916, **109**, 597—603. Compare T., 1913, **103**, 795).—The authors have examined the aqueous solution produced when cupric thiocyanate under water undergoes spontaneous transformation into cuprous thiocyanate (compare Claus, *J. pr. Chem.*, 1838, [i], **15**, 401; Meitzendorff, *Ann. Phys. Chem.*, 1842, [ii], **56**, 88). The cupric salt was obtained by precipitation of cupric chloride or acetate with excess of potassium thiocyanate solution, and the transformation was found to be complete in ten to twenty days. If the former cupric salt is used, the other products of the decomposition are carbon dioxide, ammonia, hydrogen cyanide, thiocyanic and sulphuric acids (compare Meitzendorff, *loc. cit.*), together with carbamide and possibly a trace of hydrogen sulphide, which could be attributed to the formation and hydrolysis of a minute quantity of carbonyl sulphide during the decomposition of the cupric salt. The quantity of these products, excepting the last, was determined, and the probable absence of any others was demonstrated by the ratio of the total amounts of carbon, nitrogen, and sulphur having the value 1:1:1. When cupric acetate is used for the formation of the cupric thiocyanate, cyanogen occurs as an additional decomposition product of the cupric salt.

A set of four concurrent reactions is suggested for the representation of the quantitative course of the decomposition, and this view of the change is confirmed by the acidity developed during the transformation agreeing closely with that calculated on the basis of the four equations. D. F. T.

The Nitrile of Vinylacetic Acid. PAUL HENRY (*Rep. Brit. Assoc.*, 1915, 386).—A substance, believed to be *vinylacetonitrile*, $CH_2{:}CH{\cdot}CH_2{\cdot}CN$, has been prepared by heating a mixture of allyl iodide and anhydrous cuprous cyanide for several hours at 120°. The product has b. p. 118°, and has no smell of an *iso*nitrile. Oxidation by means of neutral permanganate fails to give malonic acid, the reaction probably proceeding too far. Alkyl magnesium bromides yield only resinous products. The product of the action of ozone has the composition of the required ozonide, and does not yield acetaldehyde with water, as does the ozonide of crotononitrile. C. H. D.

Allotropy of Cyanogen. J. W. TERWEN (*Zeitsch. physikal. Chem.*, 1916, **91**, 469—499).—Cyanogen, prepared by heating a mixture of 250 grams of mercuric cyanide and 330 grams of mercuric chloride at 280° in an evacuated apparatus, was solidified in a vessel cooled by solid carbon dioxide and alcohol. This substance, from freezing-point determinations and from the *PX* dia-

gram, was shown to be impure, due to the presence of nitrogen, this gas being extremely soluble in solid cyanogen. The product was purified by repeated sublimation and removal of the first portion of the gas formed. The pure product melted at $-27\cdot92°$, but when heated up and suddenly cooled exhibited a somewhat lower melting point. This behaviour indicates the presence of two types of molecules in cyanogen, which, when in equilibrium, give a melting point of $-27\cdot92°$, the lower melting points being those of mixtures of the two types of molecules which are not present in the equilibrium quantities. The vapour pressure of cyanogen has been determined from $-78°$ to the critical temperature, $126\cdot55°$. It is shown in this connexion that a triple point exists at $-27\cdot92°$ and $55\cdot50$ cm. pressure; the boiling point at 760 mm. lies at $-21\cdot35°$, and at $0°$ the vapour pressure is $184\cdot10$ cm. The critical pressure is $58\cdot2$ atms. These values are compared with those of other observers, and the differences attributed to the difference in purity of the materials examined. It is shown that paracyanogen does not dissolve to a measurable extent in liquid cyanogen. Attempts to measure the vapour pressure of paracyanogen were abandoned owing to the decomposition of either cyanogen or paracyanogen in the preparation of the latter, and the consequent impossibility of obtaining the necessary equilibrium for measurement. The vapour pressure of paracyanogen, although not exactly determinable, is less than that of cyanogen; the relationships as far as they were obtained are expressed in *TX* and *TP* diagrams, and are in accordance with Smit's theory of allotropy. It is shown to be likely that three types of molecules of cyanogen exist—α, β, and γ. Paracyanogen is composed chiefly of β-cyanogen, and probably cyanogen consists of α- and γ-cyanogen. J. F. S.

Hydrogen Peroxide as a Hydrolytic Agent. J. V. DUBSKY (*J. pr. Chem.*, 1916, [ii], **93**, 137—142).—A modification of the hydrogen peroxide method for hydrolysing nitriles has been applied to some refractory compounds (compare Radziszewski, 1885, and Deinert, 1895).

o-Toluonitrile and α-naphthonitrile may be converted into the amides if a large excess of 3% hydrogen peroxide is used, whereas Deinert reported that they remained unchanged when treated with the usual quantity. Acetodinitrile in alcoholic solution is not hydrolysed, but gives 3 : 5-dicyano-2 : 4 : 6-trimethyl-1 : 4-dihydropyridine, m. p. 181°, which is the product of the condensation of the dinitrile with acetaldehyde. When a solution of potassium ferricyanide (2·5 grams in 225 c.c.) is heated for some hours at 40—60° with perhydrol (25 grams) it becomes dark brownish-red, and pale brownish-red, long, narrow plates crystallise out on evaporation. These have the same composition as potassium ferricyanide, but their solutions are almost opaque. It is suggested that the compound may be intermediary between the recognised isomerides of the ferricyanide, thus: $K_3Fe(C⋮N)_6 \longrightarrow K_3Fe(C⋮N)_3(N⋮C)_3 \longrightarrow K_3Fe(N⋮C)_6$. J. C. W.

Action of Ureides on Ethyl Diazoacetate. III. G. CALCAGNI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 643—648. Compare this vol., i, 207).—The author has investigated the decomposition of ethyl diazoacetate in presence of parabanic acid, alloxan, alloxantin, uric acid, theobromine, and caffeine. With uric acid the action is extremely slow and with theobromine still slower, and caffeine exerts no action. The other three compounds exhibit measurable effects, and the velocity constants have been determined and the corresponding hydrogen-ion concentrations calculated. These results are in agreement with measurements of the electrical conductivities. T. H. P.

Constitution of Gustavson's Hydrocarbons, Vinyltrimethylene and Ethylidenetrimethylene. O. PHILIPOV (*J. pr. Chem.*, 1916, [ii], **93**, 162—182).—Gustavson obtained "vinyltrimethylene" by the action of zinc dust on the compound, $C(CH_2Br)_4$, in aqueous-alcoholic solution, and transformed it into "ethylidenetrimethylene" by the addition and subsequent elimination of hydrogen iodide (A., 1896, i, 669). From time to time the constitution of these hydrocarbons has been discussed, but it is now proved that they are respectively methylene*cyclo*butane and methyl*cyclo*butene:

$$CH_2{:}C{<}{}^{CH_2}_{CH_2}{>}CH_2 \quad \text{and} \quad CMe{\lessdot}{}^{CH-}_{CH_2}{>}CH_2,$$

and that, indeed, Gustavson's original "vinyltrimethylene" was a mixture of the two, in the proportion of about 2:1. The work was completed in 1913, and accounts have appeared in the minutes of the Russian Phys. Chem. Soc. (1912–1914), but Faworski and Batalin, who came to the same conclusion, but with slight evidence (A., 1914, i, 815), made no mention of this.

Large quantities (500 grams) of the bromide can be safely reduced if only traces of alcohol are employed, and the mixture of products can be separated by fractionation with a 30-bulb column (185 cm. long). The higher fraction consists of methylene*cyclo*butane, and has b. p. 41·5°, D_4^{23} 0·7360, n_D^{23} 1·41738. This was oxidised by permanganate and aqueous acetone in the cold, and, after filtering, and removing the solvent, the residual solution of the glycol was oxidised by means of chromic acid, when succinic, formic, acetic, glutaric, and traces of oxalic acids, and *cyclo*butanone were identified among the products. An explanation of the production of glutaric acid presented some difficulty, but there is sufficient evidence in support of the view that the 4-ring may change into a 5-ring, thus:

$$CH_2{<}{}^{CH_2}_{CH_2}{>}C{:}CH_2 \longrightarrow CH_2{<}{}^{CH_2}_{CH_2}{>}C(OH){\cdot}CH_2{\cdot}OH \longrightarrow$$

$$CH_2{<}{}^{CH_2}_{CH_2}{>}C(OH){\cdot}CHO \longrightarrow$$

$$CH_2{<}{}^{CH_2\cdot CO}_{CH_2\cdot CH\cdot OH} \longrightarrow CH_2{<}{}^{CH_2\cdot CO_2H}_{CH_2\cdot CO_2H}\cdot$$

The normal course of the oxidation would be as follows:

$$CH_2{<}{CH_2 \atop CH_2}{>}C(OH)\cdot CH_2\cdot OH \longrightarrow$$

$$CH_2{<}{CH_2 \atop CH_2}{>}CO + H\cdot CO_2H \longrightarrow C_2H_4(CO_2H)_2.$$

The lower fraction, methyl*cyclo*butene, b. p. 37—39°, D_4^{23} 0·7075, n_D^{23} 1·40335, yielded succinic and lævulic acids on oxidation, thus:

$$CH_2{<}{CMe \atop CH_2}{>}CH \longrightarrow CH_2{<}{CMe(OH) \atop CH_2}{>}CH\cdot OH \longrightarrow$$

$$COMe\cdot CH_2\cdot CH_2\cdot COH \longrightarrow C_2H_4(CO_2H)_2.$$

The oxidation of the tertiary alcohol, 1-methyl*cyclo*butanol, which Gustavson obtained by various methods from his hydrocarbons, has also been studied (compare Demjanov, A., 1913, i, 451), and *cyclo*butanone, and formic, acetic, succinic, and malonic acids have been identified among the products. The oxidation of 1-methyl*cyclo*hexanol was investigated for purposes of comparison, and this was found to yield *cyclo*hexanone, and formic, acetic, adipic, glutaric, and oxalic acids. In both cases, therefore, the oxidation follows the same courses, the chief reaction necessitating the rupture of the ring on both sides of the *tert.*-carbinol group, thus:

$$(CH_2)_n{<}{CH_2 \atop CH_2}{>}CR\cdot OH \begin{cases} \nearrow (CH_2)_n(CO_2H)_2 + R\cdot CO_2H \\ \searrow (CH_2)_n{<}{CH_2 \atop CH_2}{>}CO + H\cdot CO_2H \end{cases}$$

The two hydrocarbons would, of course, yield the same hydrocarbon on reduction, which explains why various workers have obtained a homogeneous liquid with concordant physical constants from Gustavson's mixture. The reduction product is methyl*cyclo*butane. This, and the isomeric ethyl*cyclo*propane, have been prepared for comparison by Kishner's method (1911–1912; A., 1913, i, 1161, etc.). Acetylpropyl alcohol (Lipp, A., 1889, 843) was converted into acetyltrimethylene, and the hydrazone of this was distilled with potassium hydroxide in the presence of platinum, when ethyl*cyclo*propane was obtained with b. p. 36·5—37°/755 mm., $D_4^{18\cdot25}$ 0·6884, $n_D^{18\cdot25}$ 1·37973, thus:

$${CH_2 \atop CH_2}{>}CHAc \longrightarrow {CH_2 \atop CH_2}{>}CH\cdot CMe{:}N\cdot NH_2 \longrightarrow {CH_2 \atop CH_2}{>}CHEt.$$

Similarly, *cyclo*butanealdehyde was converted through the hydrazone into methyl*cyclo*butane, b. p. 36—36·5°/755 mm., D_4^{18} 0·6950, n_D^{18} 1·38473, which agrees closely with the data for the product of the reduction of Gustavson's mixture (Zelinsky, Philipov, Demjanov, 1909–1912). Methyl*cyclo*butane yielded *iso*pentane on reduction by Sabatier and Senderens's method. Attempts were also made to prepare methyl*cyclo*butane from αδ-dibromopentane (b. p. 91—93°/20 mm., $D_4^{17\cdot2}$ 1·6731, $n_D^{17\cdot2}$ 1·50911), which was obtained by the action of hydrogen bromide on γ-pentyleneglycol (b. p. 133·5°/

30—32 mm., $D_4^{16\cdot8}$ 0·9960, $n_D^{16\cdot8}$ 1·44388) (Lipp, *loc. cit.*). When boiled with sodium and xylene, the dibromide yielded a mixture of *n*-pentene, piperylene, and pentane (compare Perkin and Colman, T., 1888, **53**, 201), whilst the action of zinc dust on an alcoholic solution resulted in the formation of very pure *n*-pentane. A further proof of the absence of a trimethylene ring in the reduction product, methyl*cyclo*butane, is the fact that the hydrocarbon is recovered unchanged after passing slowly over alumina at 326°.

J. C. W.

Production of Aromatic Hydrocarbons from Paraffin Wax. GUSTAV EGLOFF and THOMAS J. TWOMEY (*J. Physical Chem.*, 1916, **20**, 515—521).—A number of experiments on the effect of heat and pressure on paraffin wax have been made with the object of ascertaining whether aromatic hydrocarbons could be produced from paraffin wax. It is shown that it is possible to produce benzene, xylene, and toluene by "cracking" paraffin wax at 600° and atmospheric pressure, also at 500° and 600° under a pressure of 150 lb. Under the same conditions of cracking aromatic hydrocarbons also result from petroleum oils of the paraffin type. The formation of aromatic hydrocarbons is not to be ascribed entirely to the decomposition of those constituents of the petroleum which contain the phenyl group. It is further shown that oils containing paraffin wax are adapted for the commercial production of benzene and toluene.

J. F. S.

Benzene: Its Solidifying and Melting Points. ROBERT MELDRUM (*Chem. News*, 1916, **113**, 266—267).—A specimen of benzene solidified at 3·92°; as the recorded values for the solidifying point of benzene vary from 0° to 5°, it is an open question whether the specimen examined by the author was pure or whether it and other specimens, on keeping, undergo changes which affect the solidifying point. At the moment of solidification a quantity of fine crystals, amounting to about 10% of the whole, was precipitated. These crystals were separated and dried at 3° between filter-paper; they melted at 5·70°, and solidified at 5·60°. The slow rate at which benzene crystallises completely, and the formation, under certain conditions, of solid colloidal benzene free from crystalline structure, would seem to indicate that benzene exists in one or more modifications.

W. P. S.

Nitration of Toluene. E. J. HOFFMAN (*J. Soc. Chem. Ind.*, 1916, **35**, 655—656; from *U.S. Bureau of Mines, Met. and Chem. Eng.*, 1916, **14**, 467—468).—The following method gave the most satisfactory results for the preparation of trinitrotoluene. To a mixture of 73·4 grams of nitric acid (D 1·42) and 146·8 grams of sulphuric acid (D 1·84) are added gradually with constant stirring 50 grams of toluene (99% purity, D_4^{20} 0·8659, yielding 88·4% between 109·4° and 110·1°, and about 97% between 108·4° and 110·1° with a Hempel still-head), the temperature being kept below 30°. When the temperature ceases to rise after all the toluene has been added

the mixture is kept for half an hour and the spent acid then drawn off. The crude mononitrotoluene (80—83 grams) is dissolved in 109·2 grams of sulphuric acid (D 1·84), the solution heated to 50°, and a mixture of 54·6 grams each of sulphuric acid and nitric acid (D 1·5) gradually added during a period of one hour, the temperature being kept below 100°, and then maintained at 90—100° for two hours, at the end of which time 145·6 grams of 15% oleum are slowly added, followed by a mixture of 72·8 grams each of 15% oleum and nitric acid (D 1·5). The temperature must not exceed 115° during this operation, and it is maintained at 90—115° for two hours subsequently. After keeping for eighteen hours the spent acid is drawn off, the crude trinitrotoluene crushed, and washed first with cold water and then several times in the molten state with hot water. A yield of 75% of the theory of trinitrotoluene, m. p. 78—80°, is obtained, and a further 8·5%, of m. p. 69—75°, can be recovered from the spent acid. If the product is purified by recrystallising from, or washing with, a mixture of 9 vols. of 95% alcohol and 1 vol. of benzene, the yield is 69% melting at 79—81°, and 7·5% melting at 78—81°. G. F. M.

Preparation of *N*-alkyl Derivatives of Organic Bases. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 291222; from *J. Soc. Chem. Ind.*, 1916, **35**, 654).—The formaldehyde used for the preparation of *N*-methyl derivatives (D.R.-P., 287802; this vol., i, 326) may be replaced by other aldehydes. Thus the action of phenylacetaldehyde on dimethylamine in presence of *iso*propyl alcohol results in the production of a quantitative yield of phenylethyldimethylamine. G. F. M.

The Stereochemistry of Quinquevalent Nitrogen. IV. The Absorption Spectra of Quaternary Ammonium Compounds. Non-equivalence of the Five Valencies of Quinquevalent Nitrogen. SHIGERU KOMATSU (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1916, **1**, 303—317).—The author has shown (this vol., i, 31) that phenylbenzylmethylallylammonium compounds exist in α- and γ-forms, the difference of which is supposed to lie in the arrangement of the groups composing their molecules. Since compounds differing merely in relative arrangement of radicles usually give similar, whilst those differing in structure usually give dissimilar ultra-violet absorption spectra, this criterion has been applied to the quaternary ammonium compounds, in the hope that the results might throw some light on the manner of combination of the groups attached to the quinquevalent nitrogen atom and also on the nature of the five valencies. The absorption spectra of *N*/100- and *N*/1000-solutions, for thicknesses between 100 mm. and 1 mm., for several substances of this type, have been examined. The hydrochlorides of ψ-cumidine and benzylamine show two absorption bands, whilst benzylethylamine and ethylaniline show only one. For each pair the heads of the bands are in slightly different positions. For α-*d*-phenylbenzylmethylallylammonium *d*-camphorsulphonate, α-*d*-phenylbenzylmethylallylammonium bromide, and

γ-*d*-phenylbenzylmethylallylammonium *d*-camphorsulphonate, the curves are very similar to each other and to those for ammonium salts, as are also the absorption curves for *l*-phenylbenzylmethyl-*n*-propylammonium bromide and chloride.

The effect of change of constitution was observed by substituting the $\cdot CH_2\cdot CO\cdot O\cdot C_2H_5$ group for the allyl group of the former series, curves for phenylbenzylmethyl(ethylacetate)-ammonium bromide and *d*-camphorsulphonate being given. They differ little from the others, and much the same remark applies to the curve for phenylbenzylhydrazonium *d*-camphorsulphonate (see Singh, T., 1914, **105**, 1972), except that the substitution of the NH_2 for the allyl group causes a slight shift of the absorption band towards the violet. The curve for phenylmethylethylhydroxylammonium chloride shows two bands. The author concludes that his α- and γ-compounds are stereoisomeric, and not structurally isomeric, and thinks that in the quinquevalent nitrogen atom the four valencies attached to alkyl groups differ from the fifth, which is attached to the negative group. For this latter view he finds support in the fact that methylethylaniline with hydrogen peroxide gave phenylmethylethylammonium oxide (Meisenheimer, *Ber.*, 1908, **41**, 3966), which with hydrochloric acid gave phenylmethylethylhydroxylammonium chloride, the aqueous solution of which on distillation gave methylethylaniline, hydrochloric acid, and oxygen. On the other hand, the action of hypochlorous acid on methylethylaniline possibly yields a phenylmethylethylhydroxylammonium chloride isomeric with the former, since on distillation it gives rise, as one of the reaction products, to a secondary amine assumed to be ethyltrichloroaniline. T. S. PA.

Scission of Racemic Alcohols by means of Camphoric Anhydride. L. MASCARELLI and (MISS) DARIA DELIPERI (*Gazzetta*, 1916, **46**, i, 416—430).—Attempts have been made to resolve synthetic decahydro-β-naphthol into its optical isomerides by Pickard's method, camphoric anhydride being employed; it is found, however, that the esterification proceeds abnormally, and gives rise to secondary products to be investigated later. Experiments on the esterification of phenylethylcarbinol (and phenylmethylcarbinol) by camphoric acid in presence of gaseous hydrogen chloride show that almost the whole of the alcohol becomes converted into the chloro-derivative, $CHPhCl\cdot CH_2Me$. Esterification in presence of sulphuric acid gave very poor yields, the alcohol undergoing dehydration to propenylbenzene, $CHPh{:}CHMe$, which was then transformed into polymerides with high boiling points. The action of silver camphorate on chloropropylbenzene also gave only small proportions of ester (compare Pickard, Lewcock and Yates, P., 1913, 127).
T. H. P.

2-Hydroxy-1-keto-4-methylene-1 : 4-dihydronaphthalene. HARRY FITZGIBBON DEAN and MAXIMILIAN NIERENSTEIN (T., 1916, **109**, 593—597).—In connexion with the investigation of purpurogallin (Nierenstein and Spiers, A., 1913, i, 1367; Dean and Nieren-

stein, A., 1914, i, 60), the authors have prepared 2-*hydroxy*-1-*keto*-4-*methylene*-1 : 4-*dihydronaphthalene*, $\begin{matrix} OH\cdot C{=\!=}CH \\ CO\cdot C_6H_4 \end{matrix}\!\!>\!C{:}CH_2$, by heating 2-hydroxy-1-keto-4-dicarbethoxymethylene-1 : 4-dihydronaphthalene (Sachs and Craveri, A., 1905, i, 909) with pyridine for eight to ten hours; the product forms deep red needles, m. p. 248—250°, but its solutions are turned blue by alkali (see Walpole, A., 1915, ii, 61). When oxidised with dilute nitric acid, 2-hydroxy-1-keto-4-methylene-1 : 4-dihydronaphthalene yielded dihydroxyhemimellitic acid identical with the product obtained in a similar manner from purpurogallin; distillation with zinc dust gave rise to naphthalene, the elimination of the methyl group agreeing with the experience of Hooker (T., 1896, **69**, 1355) when working with lapachol.

When the mixture obtained by heating 2-hydroxy-1-keto-4-methylene-1 : 4-dihydronaphthalene with acetic anhydride and a trace of sulphuric acid is poured into alcohol, the product obtained is the *acetyl* derivative, $C_{11}H_7O_2Ac$, long, lemon-yellow needles, m. p. 212—213° (decomp.; *phenylhydrazone*, $C_{13}H_{10}O_2{:}N\cdot NHPh$, dark red needles, m. p. 278—281° with decomp.), but if the mixture is poured into water, 1-*hydroxy*-2-*acetoxynaphthyl*-4-*carbinol*,

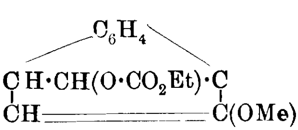
$$\begin{matrix} OAc\cdot C{-}CH \\ \| \\ OH\cdot C\cdot C_6H_4 \end{matrix}\!\!>\!C\cdot CH_2\cdot OH,$$

colourless needles, m. p. 189—190°, is produced. This substance is also obtained when a solution of 2-acetoxy-1-keto-4-methylene-1 : 4-dihydronaphthalene in acetic acid is successively treated with dilute sulphuric acid and water.

2-*Methoxy*-1-*keto*-4-*methylene* - 1 : 4 - *dihydronaphthalene*, yellow needles, m. p. 184—185° (*phenylhydrazone*, deep red plates, m. p. near 254—257°, decomp.), obtained by the action of diazomethane on the hydroxy-compound in ethereal suspension, when dissolved in acetic acid and then successively treated with dilute sulphuric acid and water, is converted into 1-*hydroxy*-2-*methoxynaphthyl*-4-*carbinol*, $OH\cdot C_{10}H_5(OMe)\cdot CH_2\cdot OH$, colourless needles, m. p. 172—173°; this undergoes methylation by diazomethane with formation of 1 : 2-*dimethoxynaphthyl*-4-*carbinol*,

$$C_{10}H_5(OMe)_2\cdot CH_2\cdot OH,$$

colourless needles, m. p. 148—150°, and in ethereal solution condenses with an equimolecular proportion of 1-keto-2-methoxy-4-methylene-1 : 4-dihydronaphthalene, yielding the corresponding *quinhydrone*, brown prisms, m. p. 219° (decomp.). The ketomethoxymethylenedihydronaphthalene compound also reacts with ethyl chlorocarbonate and sodium hydroxide, forming 2-*methoxy*-1 : 4-*ethylcarbonatomethylenenaphthalene* (annexed formula), colourless, silky needles, m. p. 126—127° (the constitution of which is demonstrated by the regeneration of the parent substance on warming with dilute pyridine or dilute acetic acid), and is reduced by sodium amalgam to 2-*methoxy*-1 : 4-*methylenenaphthalene*, glistening needles, m. p.



208° (decomp.; *benzylidene* derivative, rosettes of prisms, m. p. 224—226° decomp.). D. F. T.

Some Reactions Resulting in the Cleavage of Polynuclear Aromatic Compounds. E. P. Kohler and R. H. Patch (*J. Amer. Chem. Soc.*, 1916, **38**, 1205—1216).—Clarke and Esselen (A., 1911, i, 725; 1914, i, 278) have shown that by the action of bromine on *p*-aminobenzhydrol or one of its derivatives, a mixture of an aldehyde and a bromo-substituted aniline is produced, in accordance with an equation of the following type: $OH{\cdot}CHPh{\cdot}C_6H_2Br_2{\cdot}NH_2 + Br_2 = C_6H_5{\cdot}CHO + C_6H_2Br_3{\cdot}NH_2 + HBr$. The compounds studied by Clarke and Esselen were all diphenylcarbinol derivatives, but Clarke and Patch (A., 1912, i, 696) extended the reaction to triphenylcarbinol derivatives and to amino-alcohols with aliphatic as well as aromatic groups.

In continuation of this work, it has been found that fission of the molecule is produced, not only by halogens, but also by nitric acid, nitrous acid, and other reagents; for example, nitrous acid reacts with *p*-dimethylaminobenzhydrol, thus:

$$OH{\cdot}CHPh{\cdot}C_6H_4{\cdot}NMe_2 + HNO_2 = C_6H_5{\cdot}CHO + H_2O + NO{\cdot}C_6H_4{\cdot}NMe_2.$$

It is also shown that the fission is not confined to benzhydrols containing an amino- or substituted amino-group, but that any group which promotes substitution in the benzene nucleus will also promote fission; different groups, however, are not equally effective. When the reaction is so rapid that for each molecule of the benzhydrol 1 molecule of bromine or other reagent disappears as quickly as it is added, fission and substitution result almost exclusively. When the reagent disappears more slowly and less completely, fission and substitution decrease in favour of formation of an ether from 2 mols. of the benzhydrol or of oxidation of the benzhydrol to the corresponding ketone. The efficiency of different groups in promoting fission decreases in the order: NMe_2, OH, OMe, Me, Br. Substitution in the ortho-position to these groups diminishes the relative amount of fission, and di-substitution in this position usually inhibits it entirely.

By the action of nitrous acid on *p*-dimethylaminobenzhydrol, benzaldehyde and nitrosodimethylaniline are produced. The reaction between nitric acid and *p*-dimethylaminobenzhydrol results in fission of the molecule to the extent of 28%; owing to the oxidising action of nitric acid, the proportion of cleavage products is less than with other reagents.

Di-*p*-dimethylaminophenylethylcarbinol, $(NMe_2{\cdot}C_6H_4)_2CEt{\cdot}OH$, m. p. 118°, prepared by the action of magnesium ethyl bromide on Michler's ketone, is a crystalline substance; it reacts with bromine with formation of *p*-bromodimethylaniline in quantity indicating that fission has taken place to the extent of 67%. When *p*-dimethylaminophenyl-α-naphthylcarbinol (Sachs, A., 1905, i, 202) is treated with bromine, naphthaldehyde and *p*-bromodimethylaniline are produced.

3-*Bromo-4-dimethylaminodiphenylmethylcarbinol*,
$NMe_2 \cdot C_6H_3Br \cdot CPhMe \cdot OH$,
obtained as an oil by the action of magnesium methyl iodide on bromodimethylaminobenzophenone, yields a crystalline *oxalate*; on treatment with bromine, 53% of the carbinol undergoes fission with formation of acetophenone. When the carbinol is treated with nitrous acid, no cleavage products can be detected.

By the action of bromine on *p*-hydroxybenzhydrol, benzaldehyde and 3 : 5-dibromo-4-hydroxydiphenylcarbinol are produced in quantities representing from 33% to 42% of the carbinol used. Anisyl alcohol is converted by bromine into formaldehyde and bromoanisole. *p*-Methoxybenzhydrol, m. p. 60°, reacts with bromine with formation of benzaldehyde and *p*-bromoanisole, fission taking place to the extent of about 20%. By the action of nitric acid on *p*-methoxybenzhydrol, benzaldehyde and *p*-nitroanisole are produced, together with *nitromethoxybenzhydrol*,
$OMe \cdot C_6H_3(NO_2) \cdot CHPh \cdot OH$,
m. p. 104°, which forms pale yellow needles.

p-*Methoxybenzhydryl ethyl ether*, $OMe \cdot C_6H_4 \cdot CHPh \cdot OEt$, b. p. 258—260°/25 mm., is obtained as a gummy solid by the action of magnesium phenyl bromide on anisaldehyde; bromine and nitric acid both react with this compound with formation of benzaldehyde and bromoanisole in quantities equivalent to about 10% of the original substance.

3-*Bromo-4-methoxybenzhydrol*, $OMe \cdot C_6H_3Br \cdot CHPh \cdot OH$, m. p. 79°, obtained by the action of magnesium phenyl bromide on bromoanisaldehyde, is a crystalline compound, and when treated with bromine yielded benzaldehyde in amount equivalent to 7·5% of the original substance. 3 : 5-Dibromo-4-hydroxybenzhydrol does not show any evidence of fission when treated with either bromine or concentrated nitric acid.

When bromine is added to a solution of phenyltolylcarbinol in chloroform, very little benzaldehyde is produced, but phenyltolylcarbinyl ether, m. p. 105°, is formed. E. G.

Oxycholesterol and its Ester. II. I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1915, **96**, 342—354. Compare A., 1914, i, 683).—The *dibenzoate* of oxycholesterol is prepared by digesting oxycholesterol with excess of benzoic anhydride at 50—60° for twenty-four hours. It is separated from the excess of anhydride by treatment with methyl alcohol, in which the dibenzoate is only very slightly soluble. The product is an amorphous, yellow mass, which gives all the reactions of the mother substance, oxycholesterol, and does not have any definite melting point.

The percentage of oxycholesterol in the new compound is estimated by measuring the intensity of the bands in the spectrum after treatment with acetic and sulphuric acids and ferric chloride (*loc. cit.*), and also by hydrolysing the substance with alcoholic potassium hydroxide and weighing the liberated oxycholesterol; in both cases the results indicate the presence of a dibenzoate.

The formation of a dibenzoate together with the other properties

of oxycholesterol confirms the view that this compound contains two hydroxyl groups, and, therefore, is not identical with the α- and β-cholesterol oxides described by Westphalen (*Ber.*, 1915, **48**, 1064), in which the additional oxygen atom is linked with two carbon atoms in an "oxide" ring. The neutral oxygenated cholesterol detected in the liver (A., 1914, i, 1019), which is not oxycholesterol, is also different, judging from its colour reactions, from Westphalen's oxides. H. W. B.

Naphthenic Acid. L. G. RADCLIFFE and A. A. POLLITT (*J. Soc. Dyers*, 1916, **32**, 160—168).—The paper comprises a summary of already published work on this subject, together with an account of further experiments on the separation of individual substances from commercial naphthenic acid, and the preparation and properties of various metallic salts obtained from the commercial acid. The methods of separation tried comprised fractional distillation of the acid itself, fractional distillation of the methyl esters, and attempts to prepare and isolate crystalline acid amides. No fractions of constant boiling point could be obtained by either of the first two methods, but the acid and saponification values of the fractions indicated the presence of acids of the $C_nH_{2n-2}O_2$ series from about $C_{13}H_{24}O_2$ to $C_{23}H_{44}O_2$ as the boiling points of the esters increased from about 210° to 275°. The value of salts of sulphonated naphthenic acids as emulsifying agents was investigated, and it was found that the mixed sodium and ammonium salts of an acid prepared by sulphonation with half its weight of 10% oleum formed an excellent emulsifier, whilst the sulpho-acid itself was a good substitute for Turkey red oil in dyeing. The metallic salts of naphthenic acid were mostly prepared by precipitation from an alcoholic solution of the acid neutralised with sodium hydroxide. Most of them form soft, plastic substances, many of which are soluble in light petroleum or benzene. For a detailed account of their properties the original paper should be consulted.

G. F. M.

Conversion of Aldehydes and Ketones into α-Aminonitriles and Derivatives of the Latter. R. VON WALTHER and R. HÜBNER (*J. pr. Chem.*, 1916, [ii], **93**, 119—136).—The authors have devised a useful process for the conversion of aldehydes and ketones into α-aminonitriles, which consists in leaving a solution of the carbonyl compound and the amine in glacial acetic acid with concentrated aqueous potassium cyanide. The acetic acid acts as a solvent for the hydrogen cyanide, which it liberates, and there is consequently little danger to the operator, and it also acts as a condensing agent and a crystallising medium, for the α-aminonitriles separate in the pure state.

o-Nitrobenzaldehyde and aniline were thus converted into *o-nitro-α-anilinophenylacetonitrile*, $NO_2\cdot C_6H_4\cdot CH(NHPh)\cdot CN$, pale yellow needles, m. p. 132—133°; salicylaldehyde was converted into α-anilino-*o*-hydroxyphenylacetonitrile, m. p. 119° (Knoevenagel, A., 1904, i, 990), benzaldehyde into anilinophenylacetonitrile, and

acetaldehyde into anilinopropionitrile. Similarly, *o-nitro-α-p-toluidinophenylacetonitrile*, $NO_2\cdot C_6H_4\cdot CH(CN)\cdot NH\cdot C_6H_4Me$, was obtained from *p*-toluidine and *o*-nitrobenzaldehyde, in slender, yellow leaflets, decomp. 135—137°; *anilinocyclohexanecarboxylonitrile* (*1:1-cyanoanilinocyclohexane*), from *cyclo*hexanone, in glistening, white needles, m. p. 76°; *α-anilino-α-methylbutyronitrile*,

$$NHPh\cdot CMeEt\cdot CN,$$

m. p. 43°, from methyl ethyl ketone; and *α-anilino-α-ethylbutyronitrile*, m. p. 45°, from diethyl ketone.

α-Aminonitriles have not yet received much attention except in so far as they have been hydrolysed to the corresponding acids. α-Anilino*iso*butyronitrile, prepared by the above method from acetone in large quantities, has now been studied in other directions. It forms a perchlorate, a hydrochloride, m. p. 81°, a sulphate, m. p. 100°, and a nitrate, m. p. 75°, which all crystallise well. The corresponding *α-phenylnitrosoaminoisobutyronitrile*, $NO\cdot NPh\cdot CMe_2\cdot CN$, formed pale yellow leaflets, m. p. 75°. The nitrile was also converted into the amide and then into *α-phenylnitrosoaminoisobutyramide*, $NO\cdot NPh\cdot CMe_2\cdot CO\cdot NH_2$, m. p. 142°, which was reduced by means of zinc dust and 85% acetic acid in the cold to *α-as.-phenylhydrazinoisobutyramide*,

$$NH_2\cdot NPh\cdot CMe_2\cdot CO\cdot NH_2,$$

glistening prisms, m. p. 118° (*hydrochloride*, stout needles, m. p. 206°). This gave a *benzylidene* derivative,

$$CHPh\!:\!N\cdot NPh\cdot CMe_2\cdot CO\cdot NH_2,$$

m. p. 128°, an *o-hydroxybenzylidene* compound, m. p. 153°, and a *benzoyl* derivative, m. p. 175°.

α-Anilino*iso*butyramide was dissolved in toluene and saturated with carbonyl chloride, when a deposit of the hydrochloride was obtained, together with a solution of *2:5-diketo-3-phenyl-4:4-dimethyl-3:4-dihydroglyoxaline*, $NH<\begin{matrix}CO\cdot NPh\\ |\\ CO\cdot CMe_2\end{matrix}$ which crystallised in slender, white prisms, m. p. 205°. It was also condensed with benzenediazonium chloride to *α-p-benzeneazophenylaminoisobutyramide*, $NPh\!:\!N\cdot C_6H_4\cdot NH\cdot CMe_2\cdot CO\cdot NH_2$, which formed golden-yellow, felted needles, m. p. 217°. J. C. W.

Methyl Ester of *o*-Benzoylbenzoic Acid. T. C. McMullen (*J. Amer. Chem. Soc.*, 1916, **38**, 1228—1230).—Martin (this vol., i, 481) has shown that the *o*-benzoylbenzoyl chloride prepared from the acid by means of phosphorus pentachloride is identical with that obtained by means of thionyl chloride. It is now shown that the same product can be prepared by the action of phosphorus trichloride.

Contrary to the statement of Meyer (A., 1904, i, 747), the chloride prepared in each of these three ways has been found to yield one and the same methyl ester, m. p. 51·5—51·7°, no evidence being obtained of the existence of an ester of higher m. p. E. G.

Preparation of Selenophthaleins and their Halogen Derivatives. Farbwerke vorm. Meister, Lucius, & Brüning (D.R.-P., 290540; from *J. Soc. Chem. Ind.*, 1916, **35**, 595).—Phthalins ob-

tained by the reduction of phthaleins and their halogen derivatives on treatment in suitable solvents with selenium haloids, and, if necessary, further halogenated, are converted into products which are of value as dyes and for therapeutic purposes. G. F. M.

Preparation of Anthraquinone. A. HEINEMANN (Eng. Pat., 1915, 5514; from *J. Soc. Chem. Ind.*, 1916, **35**, 627).—Anthracene in suspension in water, dilute sulphuric acid, cold acetic acid, acetone, or a mixture of acetone with water or dilute sulphuric acid, or in solution in hot acetic acid or acetone, is oxidised to anthraquinone by ozonised air. The passage for twelve hours of ozonised air at the rate of about 4 grams of ozone per hour into a suspension of 60 grams of anthracene in 1 kilogram of sulphuric acid (D 1·5—1·6) at 100° is sufficient to complete the oxidation, and the product may be isolated by diluting the liquid with an equal weight of boiling water, neutralising with sodium carbonate, and allowing the filtered solution to crystallise. G. F. M.

Preparation of 3-Nitro-2-aminoanthraquinone. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P., 290814; from *J. Soc. Chem. Ind.*, 1916, **35**, 595).—A solution of 2-aminoanthraquinone in concentrated sulphuric acid can be nitrated at low temperatures using the calculated amount of the nitrating agent, without preliminary protection of the amino-group by acetylation, etc. G. F. M.

Kermes Dye. III. OTTO DIMROTH and REINHOLD FICK (*Annalen* 1916, **411**, 315—338. Compare A., 1910, i, 487; 1913, i, 980).—Kermesic acid has been definitely proved to be 3:5:6:8-tetrahydroxy-7-acetyl-1-methylanthraquinone-4-carboxylic acid by a series of experiments based on the following synthesis of purpurin. A mixture of phthalic anhydride, hydroxyquinol triacetate, boric acid, and benzoic acid (the last is present only as a solvent, and can be replaced by an excess of the anhydride) is heated at 180° until vapours cease to be evolved, the product is dissolved in a little boiling water, and the crystals obtained after two days are purified through the zinc salt; the resulting o-2:3:5-*trihydroxybenzoylbenzoic acid*, $C_6H_2(OH)_3\cdot CO\cdot C_6H_4\cdot CO_2H$, rhombic leaflets with $1H_2O$, m. p. 230°, sintering at 220°, is converted into purpurin by heating with boric acid and concentrated sulphuric acid at 150°.

This synthetical method is also applicable to substituted phthalic acids, for example, 4-hydroxyphthalic acid and β-coccinic (5-hydroxy-3-methylphthalic) acid. The former can evidently yield either 1:2:4:6- or 1:2:4:7-tetrahydroxyanthraquinone (hydroxyflavopurpurin or hydroxyanthrapurpurin), but the former (*acetate*, needles, m. p. 202°) is obtained, since it is identical with the hydroxyflavopurpurin produced in the following manner: Dry sodium nitrite is stirred into concentrated sulphuric acid, boric acid and flavopurpurin are added, and the mixture is stirred at 160° until a sample produces a pure red coloration with alkali; the product is boiled with water, filtered, dissolved in boiling

aqueous sodium hydroxide, precipitated by hydrochloric acid, and purified through the acetyl derivative, m. p. 202° (corr.), from which the hydroxyflavopurpurin is regenerated by hydrolysis with alkali. In a similar manner anthrapurpurin is converted into hydroxyanthrapurpurin (*acetyl* derivative, m. p. 214·5° [corr.]), although in this case a temperature of 190—200° and the presence of a little water are necessary to effect the oxidation. The orientation of the hydroxyl groups in hydroxyflavopurpurin and hydroxyanthrapurpurin is definitely proved by the fact that each yields by reduction with zinc dust and acetic acid 1:4:6-trihydroxyanthraquinone, identical with the compound synthesised from 4-hydroxyphthalic anhydride and quinol.

From its complete analogy to hydroxyflavopurpurin the hydroxyanthraquinone synthesised from β-coccinic anhydride and hydroxyquinol triacetate must be 3:5:7:8-*tetrahydroxy*-1-*methylanthraquinone*, red needles (*acetyl* derivative, pale yellow needles, m. p. 185—186°).

It is well known that the absorption spectra and the dyeing properties of hydroxyanthraquinones are very trustworthy criteria of the positions of hydroxyl groups. Since hydroxyanthrapurpurin is distinguished sharply from hydroxyflavopurpurin in its absorption spectrum and its tinctorial properties on mordanted fibres, but shows the completest similarity to decarboxykermesic acid, it is extremely probable that the latter is a substituted hydroxyanthrapurpurin. The colours of alkaline solutions of hydroxyanthrapurpurin, decarboxykermesic acid, kermesic acid, and carminic acid are the same to the eye; the spectra of these solutions and also the absorption spectra in concentrated sulphuric acid show analogous structure, and the dyeing properties of these substances also indicate the close relationship between them. This deduction is supported by the fact that hydroxyanthrapurpurin (but not hydroxyflavopurpurin), when brominated under the conditions under which kermesic acid yields tribromococcin, is converted into a *tribromohydroxyanthrapurpurin*, felted needles containing 1 molecule of acetic acid, which shows a complete analogy in behaviour and colour reactions to tribromococcin. Since the tribromohydroxyanthraquinone must be 2:4:7-tribromo-3:5:6:8-tetrahydroxyanthraquinone, it follows that tribromococcin must be 2:4:7-tribromo-3:5:6:8-tetrahydroxy-1-methylanthraquinone (compare *loc. cit.*). Finally, it is shown that kermesic acid by reduction with zinc dust and acetic acid is converted, by loss of the β-hydroxyl, the acetyl, and the carboxyl groups, into 3:5:8-*trihydroxy*-1-*methylanthraquinone*, red needles, m. p. 260° (an intermediate, yellow leuco-compound is formed, which is oxidised by concentrated sulphuric acid at 120—150°). This substance, which forms an *acetyl* derivative, pale yellow needles, m. p. 179° (corr.), can also be obtained synthetically from β-coccinic anhydride and quinol diacetate or indirectly by reducing 3:5:7:8-tetrahydroxy-1-methylanthraquinone with zinc dust and acetic acid, and oxidising the resulting leuco-compound with sulphuric acid at 150°. C. S.

Degradation of Hydroxyanthraquinones to Derivatives of Naphthaquinone. OTTO DIMROTH and ERNST SCHULTZE (*Annalen*, 1916, **411**, 339—345).—Since carminic acid, which is without doubt a derivative of purpurin (compare preceding abstract), has been converted into derivatives of naphthaquinone in several different ways, it becomes desirable to ascertain whether purpurin can be oxidised to a naphthaquinone derivative. A solution of purpurin in approximately *N*/2-sodium hydroxide is treated with a few drops of 1% cobalt sulphate solution, and then gradually with perhydrol, the temperature being kept below 50°, until the colour has changed to brownish-red. The solution is then rapidly cooled, acidified with concentrated hydrochloric acid, and the brownish-red, crystalline precipitate is digested with warm dilute sodium acetate solution. The filtered extract yields by addition of solid sodium acetate the *sodium* salt, $2C_{12}H_7O_4Na,C_{12}H_8O_4$, crystals, of *2-hydroxy-3-acetyl-α-naphthaquinone*, $O\colon C_{10}H_4Ac(OH)\colon O$, yellow leaflets, m. p. 128—129°. The acid forms a *phenylhydrazone*, $C_{18}H_{14}O_3N_2$, Bordeaux red needles, m. p. 165°, and a *monosodium* salt, $C_{12}H_7O_4Na$, yellowish-brown needles, and is converted into 3-bromo-2-hydroxynaphthaquinone by boiling with an excess of bromine in glacial acetic acid. C. S.

Anthradiquinones. OTTO DIMROTH and ERNST SCHULTZE (*Annalen*, 1916, **411**, 345—350).—Lesser's 1 : 4 : 9 : 10-anthradiquinone (A., 1915, i, 420) is a mixture of the diquinone and quinizarin. The pure diquinone is obtained by oxidising a finely divided suspension of quinizarin in glacial acetic acid with lead dioxide at the ordinary temperature and precipitating with light petroleum. It forms straw-yellow needles, m. p. 211—213° (decomp.; bath at 205°), gives yellow, non-fluorescent solutions, and readily changes in water, being partly reduced to quinizarin and partly oxidised to phthalic acid. When hydrogen chloride is led into the glacial acetic acid solution in which 1 : 4 : 9 : 10-anthradiquinone has been prepared, 3-*chloroquinizarin*, ruby plates, m. p. 239—240°, is obtained. The diquinone is converted into purpurin by solution in concentrated sulphuric acid.

The oxidation of alizarin by lead dioxide in a mixture of glacial acetic acid and ether cooled in a freezing mixture yields a straw-yellow solution of the unstable 1 : 2 : 9 : 10-anthradiquinone, which has not yet been isolated. The solution oxidises potassium iodide and sulphurous acid, and yields chloroalizarin by treatment with hydrogen chloride, and purpurin by the addition of sulphuric acid. C. S.

Preparation of Condensation Products of the Anthraquinone Series containing Nitrogen (Anthraquinoneketomorpholines). FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 290983; from *J. Soc. Chem. Ind.*, 1916, **35**, 595—596).—Halogen acetyl compounds of *o*-aminohydroxyanthraquinones, or their derivatives on treatment with reagents which yield a halogen hydracid are con-

verted into the anhydrides of *o*-aminohydroxyanthraquinoneglycollic acids, which are regarded as anthraquinoneketomorpholines. They are dyes and intermediate products. As distinguished from the known anthrapyridines, coloured vats are obtained from which cotton is dyed slightly. G. F. M.

Dyes Derived from Phenanthraquinone. KSHITISH CHANDRA MUKHERJEE and EDWIN ROY WATSON (T., 1916, **109**, 617—628).—A record of attempts to prepare colouring matters from phenanthraquinone.

In an endeavour to introduce additional hydroxyl groups into 2-hydroxy- and 2:7-dihydroxy-phenanthraquinone by the action of sulphuric acid and manganese dioxide and by the action of fuming sulphuric acid, no results of value were obtained. The latter agent converted the former hydroxy-compound into *2-hydroxyphenanthraquinonesulphonic acid* (violet *barium* salt, $C_{14}H_6O_6SBa$), from which it is not possible to obtain the corresponding dihydroxy-compound by fusion with potassium hydroxide. The only new hydroxy-derivative obtained was 2:7:?-*trihydroxyphenanthraquinone*, $C_{14}H_5O_2(OH)_3$, a reddish-brown substance, no m. p. below 290° (*triacetyl* derivative, a reddish-brown, micro-crystalline powder, m. p. near 280°), which was prepared by nitrating 2:7-diacetoxyphenanthraquinone to *nitro-2:7-diacetoxyphenanthraquinone*, yellowish-brown, rhombic prisms, no m. p. below 290°; from this, *nitro-2:7-dihydroxyphenanthraquinone*,

$$C_{14}H_5O_2(OH)_2\cdot NO_2,$$

a brown powder, no m. p. below 290°, was obtained by hydrolysis, and on reduction with tin and hydrochloric acid yielded *amino-2:7-dihydroxyphenanthraquinone*, $C_{14}H_5O_2(OH)_2\cdot NH_2$, deep brown, small, rectangular plates, no m. p. below 290° (*triacetyl* derivative, $C_{14}H_5O_2(OAc)_2\cdot NHAc$, no m. p. below 295°), which could be converted by diazotisation into the trihydroxy-compound. In the possibility that acetylamino-groups might direct the nitro-group into a more favourable position than that effected in the nitration of 2:7-diacetoxyphenanthraquinone, *2:7-diacetylaminophenanthraquinone*, $C_{14}H_6O_2(NHAc)_2$, a chocolate-brown substance, no m. p. below 295°, was prepared by acetylating the corresponding diamino-compound, but the investigation in this direction is not yet completed.

In view of the exclusion of methods for the preparation of phenanthraquinone dyes by means of the sulphonic acids, bromination and nitration were resorted to as possible steps to the desired object. *Dibromonitrophenanthraquinone*, $C_{14}H_5O_2Br_2\cdot NO_2$, yellow, prismatic needles, m. p. 244—245°, and *bromodinitrophenanthraquinone*, $C_{14}H_5O_2Br(NO_2)_2$, prismatic needles, m. p. above 300°, were obtained by nitrating dibromophenanthraquinone with hot nitric acid (D 1·42) and with a hot mixture of sulphuric acid (D 1·5) and nitric acid (D 1·51) respectively. *Bromo-2-nitrophenanthraquinone*, $C_{14}H_6O_2Br\cdot NO_2$, reddish-yellow plates, m. p. above 300°, and the isomeric *bromo-4-nitrophenanthraquinone* were ob-

tained by bromination of the corresponding nitrophenanthraquinones in acetic acid at 140° and in nitrobenzene at 110° respectively. Dibromophenanthraquinone (D.R.-P., 222206) and 2:7-dibromophenanthraquinone, by heating with aniline and copper powder, were converted into the corresponding amorphous *dianilinophenanthraquinones*; these are respectively blue and bluish-black solids, not melting below 300°, which dye wool in greenish-blue and bluish-black shades. In a similar manner 2-nitroanilinophenanthraquinone, $NO_2\cdot C_{14}H_6O_2\cdot NHPh$, a bluish-black substance, no m. p. below 300°; 4-*nitroanilinophenanthraquinone*, a black, amorphous solid, no m. p. below 300°; *nitrodianilinophenanthraquinone*, $NO_2\cdot C_{14}H_5O_2(NHPh)_2$, and *dinitroanilinophenanthraquinone*, a black powder, were prepared by the action of aniline and copper powder on the corresponding bromine compounds; the four products dye wool in bluish-black, blackish, black, and greenish-black shades respectively. On treatment with sulphuric acid (D 1·84) dianilinophenanthraquinone and 2-nitroanilinophenanthraquinone were converted into the corresponding *monosulphonic acids*, which dye wool greenish-blue and olive-green respectively. *Bromo*-p-*nitroanilinophenanthraquinone*, $C_{14}H_6O_2Br\cdot NH\cdot C_6H_4\cdot NO_2$, a reddish-violet substance, no m. p. below 280°, obtained by heating dibromophenanthraquinone with *p*-nitroaniline, dimethylaniline, and a trace of copper powder, and *dibenzidinophenanthraquinone*, $C_{14}H_6O_2(NH\cdot C_{12}H_8\cdot NH_2)_2$, a black powder obtained by heating a mixture of dibromophenanthraquinone, benzidine, cupric chloride, sodium acetate, and nitrobenzene, do not dye wool.

Various acylamino-derivatives of phenanthraquinone were prepared as possible vat dyes. 2-*Benzoylaminophenanthraquinone*, $C_{14}H_7O_2\cdot NHBz$, pink needles, m. p. 295°, 2-*phthalylaminophenanthraquinone*, $C_6H_4(CO\cdot NH\cdot C_{14}H_7O_2)_2$, pale orange needles, no m. p. below 295°, and 2-*oxalylaminophenanthraquinone*,

$$C_2O_2(NH\cdot C_{14}H_7O_2)_2,$$

reddish-brown needles, obtained from 2-aminophenanthraquinone in nitrobenzene solution by the action of the corresponding acid chlorides, were all applicable as vat dyes. In a similar manner, 2:7-*dibenzoyldiaminophenanthraquinone*, $C_{14}H_6O_2(NHBz)_2$, brick-red needles, no m. p. below 295°, and 2:7-*diphthalyldiaminophenanthraquinone*, $C_6H_4{<}{\begin{matrix}CO\cdot NH\cdot C_{14}H_6O_2\cdot NH\cdot CO\\CO\cdot NH\cdot C_{14}H_6O_2\cdot NH\cdot CO\end{matrix}}{>}C_6H_4$, brick-red needles, no m. p. below 295°, were also obtained, but only the former is absorbed from the reduced vat by cotton.

2:7-*Diaminophenanthraquinonesulphonic acid*,

$$C_{14}H_5O_2(NH_2)_2\cdot SO_3H,$$

obtained by treating 2:7-diaminophenanthraquinone with fuming sulphuric acid, imparts a green shade to alum-mordanted wool. The same diamino-compound by diazotisation and subsequent coupling with phenol was made to yield *phenanthraquinone*-2:7-*bisazophenol*, $C_{14}H_6O_2(N{:}N\cdot C_6H_4\cdot OH)_2$, brown, lenticular crystals, no m. p. below 295° (*diacetyl* derivative, brick-red, rhombic prisms, m. p. 274°).

D. F. T.

Eucalyptus Australiana, Sp. Nov. ("Narrow-leaved Peppermint") and its Essential Oil. R. T. BAKER and H. G. SMITH (*J. Roy. Soc. New South Wales*, 1915, **49**, 514—525).—This eucalypt was originally regarded as a variety of *Eucalyptus amygdalina*, but further study has rendered it desirable to give it specific rank. It flourishes on the ranges of New South Wales and Victoria, in a region which has little agricultural value, and as it yields a large amount of a good oil, it is proposed to establish a permanent industry.

The most important feature of the communication is the statement that the cineole can be profitably concentrated by collecting the steam-distillate during the first hour separately. Such a fraction contains more than 70% of cineole, whereas the whole oil averages about 45%. Moreover, this portion is almost colourless, and contains mere traces of aldehydes, so that it is pure enough for pharmaceutical purposes, whilst the yield is as great as that of the whole oil in most of the other eucalypts. The phellandrene portions which collect more particularly in the later distillates appear to contain an alcohol, $C_{10}H_{17}\cdot OH$, the determination of which is reserved. J. C. W.

Picrotoxin. PAUL HORRMANN (*Annalen*, 1916, **411**, 273—314).—Confirming the statements of Sielisch (A., 1912, i, 886) and of Angelico (A., 1913, i, 69), the author finds that picrotoxinin and picrotin yield acetone by treatment with aqueous barium hydroxide or potassium hydroxide in the cold or in the hot, but the quantity obtained is less than half the amount expected, and is smaller the longer the alkaline solution is kept in the cold before being distilled.

Picrotoxinin, $C_{15}H_{16}O_6$, and picrotin, $C_{15}H_{18}O_7$, are dilactones. They are converted by an excess of aqueous alkali, by rupture of both lactone rings, into *picrotoxinindicarboxylic acid*, $C_{15}H_{20}O_8$, decomp. 163°, $[\alpha]_D^{17\cdot5}$ +31°27′ in alcohol ($c=1\cdot272$), and *picrotindicarboxylic acid*, $C_{15}H_{22}O_9$, decomp. 271°, $[\alpha]_D^{17\cdot5}$ +61°53′ in alcohol ($c=2\cdot478$) and +37°2′ in water ($c=2\cdot498$) respectively. Intermediate between these pairs of compounds are α-picrotoxinic acid, $C_{15}H_{18}O_7$, and β-picrotinic acid, $C_{15}H_{20}O_8$, respectively, which are readily converted into the dicarboxylic acids by an excess of alkali. Picrotindicarboxylic acid forms a crystalline *silver* salt,

$$C_{15}H_{20}O_9Ag_2.$$

Picrotoxinindicarboxylic acid forms a *methyl hydrogen* ester, $C_{16}H_{22}O_8$, decomp. 183°, stout prisms with $1H_2O$ from water, $[\alpha]_D^{17\cdot5}$ +39°59′ in alcohol ($c=4\cdot335$); *dimethyl* ester, $C_{17}H_{24}O_8$, m. p. 188°, $[\alpha]_D^{17\cdot5}$ +33°6′ in alcohol ($c=1\cdot536$); *ethyl hydrogen* ester, $C_{17}H_{24}O_8$, crystals with $1\frac{1}{2}H_2O$, m. p. 161° (decomp.), $[\alpha]_D^{17\cdot5}$ +39°49′ in alcohol ($c=4\cdot479$); *diethyl* ester, $C_{19}H_{28}O_8$, m. p. 132°, $[\alpha]_D^{17\cdot5}$ +37°4′ in alcohol ($c=1\cdot259$), and *silver* salt, $C_{15}H_{18}O_8Ag_2$.

Whilst picrotoxinin and picrotin, like picrotoxin itself, have strong reducing properties, the preceding products of hydrolysis, except α-picrotoxinic acid, are stable to warm Fehling's solution and ammoniacal silver oxide. β-Picrotoxinic acid, α-picrotinic acid,

and picrotoxic acid contain a lactone ring which is not attacked even by moderately concentrated alkali. They are obtained from picrotoxinin and picrotin directly by heating with 1% mineral acid or as esters by heating with alcoholic alkalis. α-Picrotoxinic acid is converted quantitatively into the β-acid by boiling for a short time with $2N$-sulphuric acid. Thus picrotoxinin and methyl-alcoholic potassium hydroxide or methoxide yield methyl picrotoxate and methyl hydrogen picrotoxinindicarboxylate and corresponding ethyl esters in well-cooled ethyl-alcoholic solution. α-Picrotinic acid, $C_{15}H_{20}O_8$, prepared by boiling picrotin with 1% hydrochloric acid for thirty-six hours, yields when heated above its m. p. in a vacuum picrotinlactone and picrotoxic acid, the latter being identical with the acid, $C_{15}H_{18}O_7$, obtained when picrotoxinin is boiled with 1% sulphuric acid for twenty-four hours. *Methyl picrotoxate*, $C_{16}H_{20}O_7$, m. p. 171·5°, $[\alpha]_D^{17\cdot5}$ +87°36′ in alcohol (c= 4·966), the *ethyl* ester, $C_{17}H_{22}O_7,\frac{1}{2}H_2O$, m. p. 143·5°, $[\alpha]_D^{17\cdot5}$ +81°12′ in alcohol (c=5·255), and the *silver* salt, $C_{15}H_{17}O_7Ag,2H_2O$, are described.

When picrotin is oxidised by alkaline potassium permanganate only one acid of the composition $C_{15}H_{20}O_8$ (decomp. 245°, increasing to 258° after purification) is obtained, not the two α- and β-picrotinic acids, decomp. 245° and 254° respectively, as stated by Angelico (A., 1909, i, 318). The acid, which is α-picrotinic acid, loses water above its m. p. and yields two products of decomposition, which agree in their properties with the products of decomposition of Angelico's two acids (*loc. cit.*), but both have the formula $C_{15}H_{18}O_7$, and are picrotoxic acid and picrotinlactone, as stated above.

When bromopicrotoxinin is converted into picrotoxinin by zinc and acetic acid the yield is only 70% (Meyer and Bruger, A., 1899, i, 226). This is due to the fact that picrotoxinin is converted into picrotoxic acid by boiling with acids. By effecting the debromination in aqueous alcoholic solution by zinc in the presence of ammonium chloride, the author has obtained a 94% yield of picrotoxinin.

The functions of all the oxygen atoms except one in picrotoxinin, picrotin, and their derivatives have been determined. Picrotoxinin contains four oxygen atoms in lactone groups and two in hydroxyl groups; picrotoxinindicarboxylic acid contains three in hydroxyl groups and four in carboxyl groups; α-picrotoxinic acid contains two in a lactone group, two in hydroxyl groups, and two in a carboxyl group; β-picrotoxinic acid contains two in hydroxyl groups and two in a carboxyl group. The corresponding derivatives of picrotin contain one more oxygen atom in the form of a hydroxyl group. The estimation of hydroxyl groups by Zerewitinoff's method gives rather unsatisfactory results, a fractional number of groups often being found and brominated derivatives not indicating any; these irregularities are attributed to steric influences.

Angelico's formulæ of picrotoxinin and picrotin (A., 1913, i, 69) do not suffice to explain the formation of the preceding compounds. Angelico deduces his formulæ chiefly by means of the ketone,

$C_{14}H_{16}O_3$, which contains three atoms of oxygen less than picrotoxinin and four less than picrotin. The author is of opinion that a fruitful discussion of formulæ can be raised only after the intermediate compounds genetically connecting picrotoxinin and picrotin with the ketone $C_{14}H_{16}O_3$ have been isolated. C. S.

Preparation of Compounds of Quinine Derivatives and Dialkylbarbituric Acids. E. MERCK (D.R.-P., 291421; from *J. Soc. Chem. Ind.*, 1916, **35**, 654).—Instead of using quinine and its salts as described in the chief patent (D.R.-P., 249908; A., 1912, i, 1013), derivatives such as hydroquinine, ethylhydrocupreine, or propylhydrocupreine may be used. The products have a stronger narcotic action than those prepared from quinine, and are much less toxic, propylhydrocupreinedipropylbarbituric acid, for example, being practically non-poisonous. G. F. M.

Preparation of Salicyloyltheobromine. E. MERCK (D.R.-P., 291077; from *J. Soc. Chem. Ind.*, 1916, **35**, 654).—Salicyloyltheobromine is prepared by the hydrolysis of an acylsalicyl [*o*-acyloxybenzoyl] derivative of theobromine obtained by the method described in the chief patent (D.R.-P., 290205; this vol., i, 500). Thus *o*-methylcarbonatobenzoyltheobromine is hydrolysed by allowing a 25% solution in cold hydrochloric acid (D 1·19) to remain for one to two hours at the ordinary temperature. The product is precipitated by the addition of ice, and after crystallisation from alcohol melts at 198—200° (decomp.). G. F. M.

Some Derivatives of Pyrrole. III. G. KARL ALMSTRÖM (*Annalen*, 1916, **411**, 350—382. Compare A., 1913, i, 1240; 1915, i, 989).—Knorr synthesised derivatives of pyrrole from β-ketonic esters and aminoketones. It is now found that aminoketones containing a secondary amino-group can be employed, but the pyrrole derivative is produced in many cases by an entirely unexpected reaction.

Ethyl acetoacetate and phenacylaniline do not condense in glacial acetic acid to form a crystalline substance, but when the two compounds are boiled together a *substance*, $C_{18}H_{15}O_2N$, yellow prisms, m. p. 111—112°, is obtained, which exhibits phenolic properties, is unsaturated towards bromine and potassium permanganate, develops a dark green coloration with alcoholic ferric chloride, forms an *oxime*, $C_{18}H_{16}O_2N_2$, almost colourless, rhombic plates, m. p. 188° (decomp.), and a *sodium* salt, and is converted into acetic acid and 1:2-diphenylpyrrole-5-one by digestion with moderately concentrated sulphuric acid. For these reasons the substance, which is also produced from methyl acetoacetate and phenacylaniline, is regarded as *5-hydroxy-4-acetyl-1:3-diphenylpyrrole*, $NPh{<}\begin{matrix}CH{=\!=}CPh\\ C(OH){:}CAc\end{matrix}$.

In a similar manner, methyl or ethyl benzoylacetate and phenacylaniline yield *5-hydroxy-4-benzoyl-1:3-diphenylpyrrole*, $C_{23}H_{17}O_2N$, pale yellow, rhombic plates, m. p. 167—168°, which

forms an *oxime*, yellow plates, m. p. 215° (decomp.), and is decomposed by sulphuric acid into benzoic acid and 1:3-diphenylpyrrol-5-one. 5-*Hydroxy*-4-*acetyl*-1-*phenyl*-3-p-*tolylpyrrole*, greenish-yellow, four-sided prisms, m. p. 100—101° (*oxime*, faintly yellow crystals, m. p. 202° [decomp.]), and 5-*hydroxy*-4-*benzoyl*-1-*phenyl*-3-p-*tolylpyrrole*, greenish-yellow, rhombic plates, m. p. 187—188·5° (*oxime*, yellow crystals, m. p. 224° [decomp.]), are obtained by boiling *p*-methylphenacylaniline with ethyl acetoacetate and ethyl benzoylacetate respectively. By heating with equal parts of water and concentrated sulphuric acid, the former is converted into acetic acid and 1-*phenyl*-3-p-*tolylpyrrole*-5-*one*, almost colourless needles, m. p. 215—217°, and the latter into benzoic acid and the same substance. Since *p*-toluic acid is not formed in the latter decomposition, the acyl group in the hydroxyacyldiarylpyrroles must have been taken from the ethyl acylacetate, not from the phenacyl- or *p*-methylphenacylaniline. This eliminates the possible alternative constitution, $NPh<\begin{matrix} C(CO_2Ar)\colon CAr \\ C(OH)=\!=CH \end{matrix}$, for the preceding hydroxypyrroles.

By heating ethyl acetoacetate and ω-aminoacetophenone in acetic acid, Knorr and Lange in 1902 obtained ethyl 3-phenyl-5-methylpyrrole-4-carboxylate. However, when the two compounds are heated together in the absence of a solvent, *ethyl*-β-*phenacylaminocrotonate*, $COPh\cdot CH_2\cdot NH\cdot CMe\colon CH\cdot CO_2Et$, colourless needles, m. p. 102—103°, is obtained, which is converted into ethyl 3-phenyl-5-methylpyrrole-4-carboxylate by boiling with glacial acetic acid.

Phenacylmethylamine and ethyl acetoacetate react when heated, either with or without glacial acetic acid, to form *ethyl* 3-*phenyl*-1:5-*dimethylpyrrole*-4-*carboxylate*, colourless prisms, m. p. 53—54°; the corresponding *acid*, $C_{13}H_{13}O_2N$, forms colourless needles, m. p. 174—175° (decomp.), and readily loses carbon dioxide by heating in glacial acetic acid, yielding 3-*phenyl*-1:5-*dimethylpyrrole*, colourless prisms, m. p. 56—57°.

Phenacyl-β-naphthylamine, which is readily prepared by adding ω-bromoacetophenone to an alcoholic solution of β-naphthylamine at about 50°, yields by boiling with ethyl acetoacetate 5-*hydroxy*-4-*acetyl*-3-*phenyl*-1-β-*naphthylpyrrole*, greenish-yellow prisms, m. p. 117—118°, which forms an *oxime*, $C_{22}H_{18}O_2N_2$, m. p. 186° (decomp.), and is converted into acetic acid and 3-*phenyl*-1-β-*naphthylpyrrole*-5-*one*, $C_{20}H_{15}ON$, faintly greenish-yellow plates, m. p. 184—185°, by heating with equal parts of water and concentrated sulphuric acid.

Phenyldiphenacylamine, m. p. 236—240° (Braun in 1908 gave 225°), is obtained by heating phenacylaniline with ethyl oxalacetate at 150° or by boiling it with an alcoholic solution of ω-chloroacetophenone.

1:3-*Diphenylpyrrole*-5-*one*, $NPh<\begin{matrix} CO-CH_2 \\ CH\colon CPh \end{matrix}$, colourless plates, m. p. 169—170°, can be obtained (1) by heating 5-hydroxy-4-benzoyl-1:3-diphenylpyrrole with sulphuric acid or with concen-

trated hydrochloric acid at 140—150°; (2) by heating 5-hydroxy-4-acetyl-1:3-diphenylpyrrole with sulphuric acid, hydriodic acid (b. p. 127°), or 99% hydrazine hydrate, or with alcoholic hydroxylamine for one hour; (3) by boiling phenacylaniline with ethyl malonate or acetonedicarboxylate. Its constitution is determined by the fact that 3-*phenyl*-1-p-*bromophenylpyrrole*-5-*one*,

$$C_{16}H_{12}ONBr,$$

colourless crystals, m. p. 207—209, obtained by brominating the substance in warm glacial acetic acid, is oxidised by hot chromic and acetic acids to *phenylmalein*-p-*bromophenylimide*,

$$C_6H_4Br\cdot N<\begin{matrix}CO\cdot CH\\ \quad\ \ \|\\ CO\cdot CPh\end{matrix},$$

golden-yellow needles, m. p. 158—159°; by hydrolysis the latter yields *p*-bromoaniline and phenylmaleic anhydride, a portion of which undergoes change to phenylfumaric acid. 1:3-Diphenylpyrrole-5-one shows no phenolic properties. It is insoluble in alkali, does not react with acetyl chloride, and does not develop a coloration with alcoholic ferric chloride. By heating with phosphorus trichloride on the water-bath, however, it yields 5-*chloro*-1:3-*diphenylpyrrole*, colourless, rhombic plates, m. p. 77—78°, which is reduced to 1:3-diphenylpyrrole by hydriodic acid (D 1·22) and red phosphorus at 130°. 1:3-Diphenylpyrrole and 1:3:5-triphenylpyrrole respond to the pine-shaving test, whereas 1:4:5- and 1:2:5-triphenylpyrroles, in which the phenyl groups are contiguous, do not.

1:3-Diphenylpyrrole-5-one gives a very poor yield of *phenylmaleinphenylimide*, $C_{16}H_{11}O_2N$, canary-yellow leaflets, m. p. 116—117°, by oxidation with hot chromic and acetic acids, but by treatment with phosphorus pentachloride and a few drops of phosphoryl chloride at 50—60°, and finally at 90°, and subsequently with water, it yields *β-chloro-α-phenylmaleinphenylimide*, $NPh<\begin{matrix}CO\cdot CCl\\ \quad\ \ \|\\ CO\cdot CPh\end{matrix}$, needles, m. p. 103—104°, which is converted into aniline and *β-chloro-α-phenylmaleic anhydride*, $C_{10}H_5O_3Cl$, colourless, rhombic plates, m. p. 83—84°. The last compound yields benzoic acid by oxidation, and therefore does not contain its halogen in a benzene nucleus.

3-Phenyl-1-*p*-bromophenylpyrrole-5-one in boiling glacial acetic acid is converted by bromine (about 4 mols.) presumably into a compound, $C_6H_4Br\cdot N<\begin{matrix}CO—CBr\\ \qquad\ \ \|\\ CBr_2\cdot CPh\end{matrix}$, since the solution by treatment with water yields *β-bromo-α-phenylmalein*-p-*bromophenylimide*, $C_6H_4Br\cdot N<\begin{matrix}CO\cdot CBr\\ \quad\ \ \|\\ CO\cdot CPh\end{matrix}$. The last substance occurs in two modifications, pale yellow plates, m. p. 105—107°, and canary-yellow prisms, m. p. 128—130°, the former being obtained from cold, the latter from warm solutions. Either modification can be obtained from a solution, however, by inoculation with that modification. Also either modification, when fused and, if necessary, supercooled, yields the other form by inoculation. The substance is decomposed by

alcoholic sodium ethoxide, yielding *p*-bromoaniline and β-ethoxy-α-phenylmaleic anhydride. C. S.

Formation of Pyridine Bases by Condensation of Ketones and Amides. AMÉ PICTET and PIERRE STEHELIN (*Compt. rend.*, 1916, **162**, 876—878; *Arch. Sci. phys. nat.*, 1916, [iv], **41**, 469—474).—Acetone (2 mols.) and acetamide (1 mol.) when heated together in sealed tubes at 250° give a very poor yield of 2:4:6-trimethylpyridine. Benzamide (1 mol.) and acetophenone (2 mols.) when similarly heated at 275° give a slightly better yield of 2:4:6-triphenylpyridine. The authors have succeeded in preparing a *picrate*, citron-yellow needles, m. p. 192·5°, of the latter compound. All attempts to prepare pyridine itself by condensing acetaldehyde and formamide were unsuccessful, but by heating together paraldehyde and acetamide at 280° a small amount of α-picoline was obtained. W. G.

Preparation of Substituted Quinoline-4-carboxylic Acids. FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P., 290703; from *J. Soc. Chem. Ind.*, 1916, **35**, 594—595).—Isatin is condensed with ketones in equivalent quantities in presence of an excess of aqueous ammonia, and the resulting amide saponified. The preparation of 2-*methylquinoline*-4-*carboxylic acid*, *tetrahydroacridine*-5-*carboxylic acid*, 2-*phenylquinoline*-4-*carboxylic acid*, and 3-*phenyl*-2-p-*tolylquinoline*-4-*carboxylic acid* is described. G. F. M.

Preparation of Acidyl Derivatives of the Xanthine Series. E. MERCK (D.R.-P., 290910; from *J. Soc. Chem. Ind.*, 1916, **35**, 654).—Acidyl derivatives of xanthines of the general formulæ X·CO·R, X·CO·R·CO·X, or X·CO·X, where X is a xanthine or mono- or di-alkyl substituted xanthine residue, and R the radicle of an alcohol, phenol, or amine containing active hydrogen, are obtained by treating metallic salts of xanthines with derivatives of chloroformic acid, or xanthine chloroformates with suitable alcohols, phenols, or amines. The products combine the diuretic action of xanthines with the therapeutic properties of the phenol, etc., as, for example, the antineuralgic action of salicylic acid or the uric acid dissolving properties of piperazine. They are fairly stable towards acids, but are easily hydrolysed by alkalis.

G. F. M.

***m*-Azoxyphenylpropiolic Acid.** S. REICH and (MLLE.) M. XIENZOPOLSKA (*Bull. Soc. chim.*, 1916, [iv], **19**, 146—151).—A further difference is noted between the two stereoisomeric α-bromo-*m*-nitrocinnamic acids (compare A., 1914, i, 41). The isomeride, m. p. 217°, when heated for three hours with alcoholic potassium hydroxide, gives *m*-nitrophenylpropiolic acid (*loc. cit.*). The isomeride, m. p. 116°, is scarcely attacked under these conditions, but if the heating is prolonged and stronger alkali is used, in addition to removal of hydrogen bromide, reduction takes place and the product is m-*azoxyphenylpropiolic acid*,

$$CO_2H\cdot C{:}C\cdot C_6H_4\cdot NO{:}N\cdot C_6H_4\cdot C{:}C\cdot CO_2H,$$

pale yellow needles, m. p. 208° (decomp.). This acid is best prepared, however, by heating $\alpha\beta$-dibromo-*m*-nitrophenylpropionic acid (*loc. cit.*) with an excess (6 mols.) of 10% alcoholic potassium hydroxide for twelve hours under reflux. It is purified by means of its *barium* salt, which is decomposed by dilute hydrochloric acid. Its *sodium* salt gives a white precipitate of a *silver* salt, which is extremely explosive when slightly rubbed or heated. The free acid dissolves in concentrated sulphuric acid, giving a deep red solution, from which water precipitates a *substance*, which is probably a *p*-hydroxyazo-compound. When oxidised in sodium carbonate solution at the ordinary temperature with dilute potassium permanganate, *m*-azoxyphenylpropiolic acid gives *m*-azoxybenzoic acid. When heated in a sealed tube with water at 130—135° for three hours, it yields m-*azoxyphenylacetylene*, pale red crystals, m. p. 101—102°. In alcoholic solution this gives with ammoniacal cuprous chloride a yellow precipitate, and with ammoniacal silver nitrate a very pale yellow precipitate. The cuprous compound is not attacked by an alkaline solution of potassium ferricyanide.

When exposed under a bell-jar to the vapours of bromine (2 mols.), *m*-azoxyphenylpropiolic acid absorbs bromine and gives *tetrabromo*-m-*azoxycinnamic acid*, brown needles, grouped in stars, m. p. 244—245°. This acid also undergoes transformation by strong sulphuric acid, giving what is probably a *p*-hydroxyazo-compound. The tetrabromo-*m*-azoxycinnamic acid when exposed anew to bromine vapours unites with four more atoms of bromine, giving a *compound*, m. p. 90—110°, extremely soluble in all organic solvents except ligroin.

When *m*-azoxyphenylpropiolic acid is reduced in sodium carbonate solution with sodium amalgam it gives m-*azocinnamic acid*, golden-yellow crystals, m. p. 168—169°. W. G.

Etherification of *o*-Hydroxyazo-compounds. VI. G. CHARRIER (*Gazzetta*, 1916, **46**, i, 404—415).—It was found by Charrier and Ferreri (A., 1914, i, 1178) that the ethers of 1-arylazo-β-naphthols exhibit far more pronounced basic properties than the corresponding *o*-hydroxyazo-compounds themselves. Thus, treatment of ethereal solutions of the ethers with ethereal hydrochloric acid results in the separation of the insoluble hydrochlorides, whilst with the hydroxyazo-compounds only intensification of the coloration occurs. In accordance with these results, various ethers of 1-benzeneazo-β-naphthol have been prepared by the action on the latter of alkyl iodides in presence of the theoretical proportion of sodium ethoxide, the ethers then being converted into their hydrochlorides and the latter separated and transformed into the free ethers by means of alkali hydroxide. 1-Benzeneazo-β-naphthol propyl, *iso*propyl, and *iso*butyl ethers, thus prepared, are well crystallised, bright red or garnet-red compounds melting undecomposed at relatively low temperatures, and exhibit properties analogous to those of the 1-arylazo-β-naphthols previously described. That they are *O*-ethers is shown by their reduction to aniline and

1-amino-β-naphthol ethers. They function as di-acid bases except towards hydrochloroplatinic acid, 1 mol. of the latter combining with 2 mols. of the base. When heated, the hydrochlorides are decomposed according to the equation:

$$OR\cdot C_{10}H_6\cdot N\colon NPh,2HCl \longrightarrow OH\cdot C_{10}H_6\cdot N\colon NPh + RCl + HCl.$$

The nitrates undergo diazo-scission when heated carefully near their melting points, $OR\cdot C_{10}H_6\cdot N\colon NPh,2HNO_3 = OR\cdot C_{10}H_6\cdot NO_2 + N\colon NPh\cdot NO_3 + H_2O$, whilst alcohols convert them into the corresponding *o*-hydroxyazo-compounds, $OR\cdot C_{10}H_6\cdot N\colon NPh,2HNO_3 \longrightarrow OH\cdot C_{10}H_6\cdot N\colon NPh + R\cdot NO_3 + HNO_3$. The ethers of 1-nitro-$\beta$-naphthol, obtained by the above diazo-scission, are new compounds, and, on reduction by means of zinc and hydrochloric acid, yield ethers of 1-amino-β-naphthol identical with those obtained by reduction of the corresponding ethers of 1-benzeneazo-β-naphthol.

In each of the three etherifications, the principal product is accompanied by a *compound*, $OH\cdot C_{10}H_6\cdot N\colon NPh,ONa\cdot C_{10}H_6\cdot N\colon NPh$ (?), which forms long, reddish-brown, almost black, prismatic needles, with metallic reflection, m. p. 219—220°, and is hydrolysed slowly by water. This compound may be related to that obtained by Betti and Leoncini (A., 1901, i, 55) by prolonged boiling of 1-benzeneazo-β-naphthol with 50% sodium hydroxide solution. Farmer and Hantzsch's salts (A., 1900, i, 122) of 1-benzeneazo-β-naphthol, obtained by the action of sodium or potassium ethoxide, exhibit green metallic reflection, and, unlike the present compound, are hydrolysed readily by water.

1-*Benzeneazo-β-naphthyl propyl ether*, $NPh\colon N\cdot C_{10}H_6\cdot OPr$, forms deep garnet-red leaflets, m. p. 40—41°, and the *hydrochloride* (+2HCl) deep red leaflets with golden reflection, m. p., with rapid heating, 100—105° (decomp.). The *nitrate* ($+2HNO_3$), m. p. 72—73° (decomp.), yields 1-*nitro-β-naphthyl propyl ether*,

$$NO_2\cdot C_{10}H_6\cdot OPr,$$

sulphur-yellow needles, m. p. 86°, when heated; 1-*amino-β-naphthyl propyl ether*, $C_{13}H_{15}ON$, forms slender, white needles, m. p. 45°, becoming red in the light, and with β-naphthol yields 1-β-*naphthol-azo-β-naphthyl propyl ether*, $OH\cdot C_{10}H_6\cdot N\colon N\cdot C_{10}H_6\cdot OPr$, which crystallises in shining, golden-bronze leaflets, m. p. 157—158°. 1-*Benzeneazo-β-naphthyl propyl ether sulphate* ($+H_2SO_4$) and *platinichloride*, $(C_{19}H_{18}ON_2)_2H_2PtCl_6$, which is a scarlet, crystalline powder, m. p. 172°, were prepared.

1-*Benzeneazo-β-naphthyl* iso*propyl ether*, $C_{19}H_{18}ON_2$, forms bright red, shining leaflets, m. p. 70°, and yields the following salts: the *hydrochloride*, slender, reddish-brown needles, melting indefinitely; the *nitrate*, reddish-brown needles, m. p. 60° (decomp.); the *sulphate*, golden leaflets; and the *platinichloride*, brick-red, microcrystalline powder, m. p. 147° (decomp.). 1-*Nitro-β-naphthyl* iso*propyl ether*, $C_{13}H_{13}O_3N$, forms slender, pale yellow leaflets, m. p. 63°.

1-*Benzeneazo-β-naphthyl* iso*butyl ether*,

$$NPh\colon N\cdot C_{10}H_6\cdot O\cdot CH_2\cdot CHMe_2,$$

forms bright red, rectangular plates, m. p. 17—18°, and gives: the *hydrochloride*, red needles with golden reflection; *nitrate*, slender,

red needles with golden reflection, m. p. 65° (decomp.); *sulphate*, metallic green leaflets; and *platinichloride*, deep red, crystalline powder, m. p. 150—151°, contracting at a somewhat lower temperature. 1-*Nitro-β-naphthyl* iso*butyl ether*, $C_{14}H_{15}O_3N$, forms aggregates of slender, straw-yellow needles, m. p. 71—72°, and 1 *amino-β-naphthyl* iso*butyl ether*, $C_{14}H_{17}ON$, slender, white leaflets, highly sensitive towards light. T. H. P.

Anticoagulating Power of Aniline Acid Dyes with Respect to Proteins. A. CH. HOLLANDE (*Compt. rend.*, 1916, **162**, 959—961).—Aniline acid dyes, such as eosin and Congo-red, combine with proteins, forming coloured acido-albumins, which are not coagulated when the solution is boiled or heated in an autoclave at 120° for twenty minutes. If the soluble protein is mixed in the requisite proportion with an acid dye, the mixture forms a jelly when heated at 100° for a few minutes. This jelly can be sterilised at 120° without losing its transparency, and can be used as a culture medium for bacteriological work if a non-toxic acid dye is used. The acid dyes vary in their anti-coagulating powers, the most active being eosin, soluble in water, then orange-G., uranine, and Congo-red. The combinations obtained by their use are precipitated in the cold by 90% alcohol, by nitric acid, or by formalin. They are also precipitated by 10% acetic acid, but are soluble in excess of the reagent. The precipitates formed have the colour of the dye used, the supernatant liquid being practically colourless. W. G.

Acetylated Proteins. K. LANDSTEINER and E. PRÁŠEK (*Biochem. Zeitsch.*, 1916, **74**, 388—393).—Various proteins were treated under different conditions with acetic anhydride, and the acetyl groups in the products so obtained were estimated by a modification of Wenzel's method. Different amounts of acetyl groups were found with the different proteins. Acetylated proteins do not give the Millon reaction, and the conclusion is drawn that the majority of acetyl groups are attached to a nitrogen atom. S. B. S.

Phylloerythrin (Bilipurpurin). HANS FISCHER (*Zeitsch. physiol. Chem.*, 1915, **96**, 292—295. Compare Marchlewski, A., 1905, i, 847).—The author finds on analysis that the empirical formula for phylloerythrin is $C_{34}H_{36}O_6N_4$. It gives a crystalline *copper* salt, $C_{36\cdot5}H_{34\cdot5}O_{3\cdot5}N_{4\cdot5}Cu$, containing a ½ mol. of pyridine. The formation of this salt and the concomitant diminution in the content of oxygen confirm Marchlewski's view that phylloerythrin is not a bile pigment, but a derivative of chlorophyll.

During the process of extraction of phylloerythrin from the fæces of the sheep, a *substance*, $C_{24}H_{34}O_2$, yellow plates from methyl alcohol, m. p. 192—193°, was isolated, which appears to be related to xanthophyll. H. W. B.

"Hæmatoporphyrin" from Urine and Bone. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1915, **96**, 183—203).—The absorption spectrum of the porphyrin in urine differs towards the violet end from

that of hæmatoporphyrin, but is practically identical with a porphyrin found in bones in four cases of osteohæmochromatosis. The presence of a new porphyrin in urine (urinoporphyrin) is therefore confirmed (compare Fischer, this vol., i, 514). H. W. B.

Urinoporphyrin. II. Cotoporphyrin. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1915, **96**, 148—182. Compare this vol., i, 514).—*Cotoporphyrin*, $C_{36}H_{36}O_8N_4$, is a substance obtained from the fæces of the patient from whose urine the similar substance, urinoporphyrin, was isolated (*loc. cit.*). It is also present in small amount in the urine, does not melt below 300°, and is insoluble in most organic solvents except pyridine. After the fat, cholesterol, etc., have been removed from the fæces by alcohol and ether, cotoporphyrin is extracted from the residue by sodium hydrogen carbonate solution. Addition of acetic acid to the extract precipitates the cotoporphyrin, which is then transformed into the methyl ester.

Trimethylcotoporphyrin, $C_{39}H_{42}O_8N_4$, needles from chloroform–methyl alcohol, m. p. 249—250°; *copper* salt, $C_{39}H_{40}O_8N_4Cu$, microscopic prisms from pyridine–acetic acid, m. p. 285·5° (corr.); *iron* salt, $C_{39}H_{40}O_8N_4FeCl$, prisms from chloroform–ether. *Triethylcotoporphyrin*, $C_{42}H_{48}O_8N_4$, long needles from alcohol, m. p. 217—220°. A *copper* salt, $C_{36}H_{34}O_8N_4Cu$, crystallising in prismatic needles, is obtained from free cotoporphyrin by mixing its aqueous solution with copper acetate in acetic acid solution.

After the crystallisation of the trimethylurinoporphyrin (*loc. cit.*), the mother liquors yield on evaporation the methyl ester of a new *porphyrin* with four carboxylic acid radicles, $C_{41}H_{44}O_{10}N_4$, m. p. 240°.

Attempts to convert urinoporphyrin or hæmatoporphyrin into cotoporphyrin by the action of fæcal bacteria were unsuccessful. After subcutaneous injection into a rabbit, cotoporphyrin appears unchanged in the urine. Urinoporphyrin similarly injected also reappears in the urine, whilst the fæces remain free from cotoporphyrin. The author inclines to the view that urinoporphyrin arises by the addition of carboxylic acid radicles to cotoporphyrin, rather than that the reverse change occurs in the animal organism.

Measurements of the lines in the spectra of the different porphyrins and their derivatives are appended. H. W. B.

Partition of Phosphorus in Thymus–Nucleic Acid. HILDEGARDE C. GERMANN (*J. Biol. Chem.*, 1916, **25**, 189—194).—The examination of thymus-nucleic acid by the method devised by Walter Jones (A., 1916, ii, 356) shows that this substance contains three (or a multiple of three) phosphorus atoms in the molecule. It is probably a tri- or hexa-nucleotide. One-third of the combined phosphoric acid is readily removed by hydrolysis, whilst the remaining two-thirds is more firmly bound. It is not known whether the phosphoric acid which is easily removed corresponds with purine groups, as is the case with yeast–nucleic acid. H. W. B.

A New Heterogeneous Chain, containing Arsenic in the Nucleus. Methyl*cyclo*pentamethylenearsine. ENRIQUE V. ZAPPI (*Bull. Soc. chim.*, 1916, [iv], **19**, 151—154).—Dichloro-

methylarsine, $AsMeCl_2$, readily reacts with the magnesium derivative of αε-dichloropentane, and on distillation *methyl*cyclo*pentamethylenearsine*, $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>AsMe$, b. p. 160°, passes over as a colourless liquid smelling strongly of oil of mustard. This compound readily oxidises in the air, the arsenic becoming quinquevalent, and gives an *oxide*, which is colourless, has a more agreeable odour, and is soluble in alkaline solutions. With methyl iodide, the original compound gives a *methiodide*, $C_5H_{10}AsMe_2I$, a white, crystalline solid, which in a sealed tube has m. p. 290°. When heated in an open tube, it decomposes, giving methyl iodide and the original arsine. In aqueous solution with silver oxide the methiodide gives the *hydroxide*, $C_5H_{10}AsMe_2\cdot OH$, which is strongly alkaline. W. G.

Physiological Chemistry.

Chemical and Physical Analysis of Blood in Thirty Normal Cases. A. O. GETTLER and WILLIS BAKER (*J. Biol. Chem.*, 1916, **25**, 211—222).—The authors have estimated the chemical constituents and have measured the physical constants of samples of blood taken from thirty normal individuals (males and females of ages ranging from seventeen to sixty). About 70 c.c. of blood were collected in each case, and, by employing modern "micro" methods as far as possible, the following estimations were made: total solids, coagulable nitrogen, non-coagulable nitrogen, ammonia nitrogen, urea nitrogen, residual nitrogen, uric acid, creatine, creatinine, chlorides, dextrose, fat, cholesterol, electrical conductivity, concentration of hydrogen ion (P_H), number of red corpuscles, number of white corpuscles, volume of corpuscles, hæmoglobin, and Wassermann test—all determined on the whole blood; nitrogen, chlorides, and volume of combined carbon dioxide in the plasma; nitrogen, specific gravity, freezing point, conductivity and refractive index of the serum. The results constitute a valuable contribution to the knowledge of the state of the blood in health.

For the estimation of the total solids, one drop of the blood is caught on a small piece (2 sq. cm.) of dried blotting-paper, which is at once placed in a wide-mouthed weighing bottle (the stopper being inserted at once to avoid evaporation) and weighed. The stopper is then tilted, the whole placed in an air-bath at 80—90°, and dried to constant weight. The solids range from 21 to 24%, two cases only being a trifle outside these limits.

An acid mercuric chloride solution is employed in the estimation of the non-protein nitrogen to remove the proteins. Five c.c. of blood are pipetted into a small Erlenmeyer flask, 5 c.c. of water added to lake the blood, then 10 c.c. of 5% hydrochloric acid; the

mixture is well shaken and 10 c.c. of 5% mercuric chloride solution added. After again shaking, the mixture is centrifugalised, the supernatant liquid filtered, and 20 c.c. of the filtrate taken for a micro-Kjeldahl estimation. The values range from 30 to 45 mg. of non-protein nitrogen per 100 c.c. of blood.

The fat and cholesterol in blood are estimated by a modification of the Soxhlet method for the estimation of fat in milk. Five c.c. of the blood are allowed to flow over a coil of fat-free absorbent paper; this is dried overnight in a vacuum desiccator containing phosphoric oxide at 50—60°. The coil is then extracted in the usual way with anhydrous ether. After the evaporation of the ether, the residue is dried to constant weight in a vacuum over phosphoric oxide. The residue thus obtained consists of fatty substances and cholesterol. The latter is estimated by dissolving the residue in chloroform and treating it with acetic anhydride and sulphuric acid, as in Autenrieth and Funk's method, the colour developed being subsequently compared in a colorimeter with that of a similarly treated standard solution of cholesterol in chloroform. The amount of cholesterol in normal blood ranges from 30 to 60 mg. in 100 c.c. of blood.

A consideration of the results reveals certain differences from those recorded by other workers; of these, only two can here be noticed. The amount of creatinine is usually under 0·1 mg. in 100 c.c. of blood, which is surprisingly low. Any value above 1 mg. is to be considered as possibly indicating a pathological condition. The amount of uric acid in the blood varies very greatly, the figures given ranging from 0·3 to 4 mg. of uric acid per 100 c.c. of blood.

H. W. B.

Influence of Hydrogen-ion Concentration on the Oxygen Dissociation Curve of Hæmoglobin. PETER RONA and ARVO YEPPÖ (*Chem. Zentr.*, 1916, i, 618—619; from *Verhandl. Physiol. Ges. Berlin*, 1915, **40**, 1—2).—The experiments were carried out with blood corpuscles from dogs, twice washed with physiological brine solution, and gaseous mixtures containing 1—15% of oxygen at 38° were employed. Increase in the acidity lowered at first the dissociation constants of the oxygen, and the combining power of the hæmoglobin decreased. In concentrated hæmoglobin solution acidities as great as $p_H = 6$ caused precipitation of protein, but this was avoided by suitable dilution with water, and it was then found that a rise in the dissociation curve set in. The authors explain this by postulating the formation of molecular aggregates at low hydrogen-ion concentrations, which as a whole can absorb less oxygen than the individual molecules. A further increase in the acidity causes these aggregates again to pass into solution, and the curve accordingly commences once more to rise. G. F. M.

The Water Constant of Blood. GUNNOR BLIX (*Biochem. Zeitsch.*, 1916, **74**, 302—311).—The changes in the water content in the blood of rabbits were measured by Bang's micro-method. During starvation, the amount of water diminishes for the first two days

and then reaches a constant low level. The effect of ingestion of water by both fed and fasting animals was investigated, and it was found that the water content did not increase more after ingestion of 25 c.c. than after 150 c.c., and that the maximal water content was attained more rapidly after the smaller quantity had been taken than after the larger amount. The influence of injections of mercuric chloride on the blood was examined and was found to lead both to hydræmia and increase of carbamide nitrogen. No satisfactory explanation of these phenomena can yet be given.

S. B. S.

The Distribution of the Residual Nitrogen between Blood Corpuscles and Plasma. IVAR BANG (*Biochem. Zeitsch.*, 1916, **74**, 294—297).—The experiments on rabbits confirm the earlier results obtained. After starvation there is an increase in the residual nitrogen of the blood, which is entirely in the carbamide fraction. Before starvation there is an equal distribution of the carbamide between plasma and corpuscles, whereas the latter contain generally more amino-acids. This distribution remains unchanged after starvation. There is no change in the amino-acid content of the blood after seven days' starvation, and this fact indicates that there is a regulatory mechanism governing the output of amino-acids from the cells of the organs to the blood, which then carries them to the liver for deamidisation. After administration of amino-acids (glycine) the change in the amino-acids is greater in the serum than in the whole blood, and this justifies the conclusion that after resorption of amino-acids from the intestine into the blood, these are found almost exclusively in the plasma. S. B. S.

Formation of Specific Proteoclastic Ferments in Response to Introduction of Placenta. FLORENCE HULTON (*J. Biol. Chem.* 1916, **25**, 227—230).—Dog's serum readily digests casein, protamine, and other proteins, including placental protein, and in most cases an increase in the digestive power of the serum after the intraperitoneal or intramuscular injection of human placental protein into the dog is not observed. The two chief exceptions to the above general rule occur (i) with protamine, which is digested readily by normal serum, and even more readily by the serum of the injected animal, and (ii) with gliadin, which is only slightly acted on by normal serum, but hydrolysed to a considerable extent by the serum of the injected dog. A specific reaction in pregnancy cannot therefore be due to increased ferment production in the blood. H. W. B.

Digestibility of Bread. I. Salivary Digestion in Vitro. J. C. BLAKE (*J. Amer. Chem. Soc.*, 1916, **38**, 1245—1260).—A study of the rate of digestion of wheaten bread has been carried out polarimetrically. Methods of recognising the various polysaccharides of wheat flour are described, and the existence of two new substances, "blue-amylose" and "cyanodextrin," is indicated.

The three chief constituents of the cereal starches are amylo-

cellulose (the wall of the granule), amylopectin, and amylose. The amylose, during salivary digestion, passes rapidly through the stages of amylodextrin and erythrodextrin, and an appreciable quantity of achroödextrin enters the solution. All the dextrins disappear within fifteen minutes, and further digestion represents action on amylocellulose and amylopectin and their hydrolytic products. The amylopectin is hydrolysed to rose-amylose, which digests completely in four hours. The amylocellulose is not digested until after twenty-four hours. The activity of amylases is not affected by small temperature changes or by the organic acids occurring in bread.

The conclusions are drawn that under ordinary physiological conditions most of the amylose is converted into dextrins in the mouth, that these dextrins and most of the amylopectin are digested in the stomach, and that the digestion of the amylocellulose takes place principally in the intestine. E. G.

The Resorption and Assimilation of Proteins and Amino-acids. IVAR BANG (*Biochem. Zeitsch.*, 1916, **74**, 278—293).—The effect of the administration by the mouth of glycine to rabbits was investigated. The increase of amino-acid nitrogen in the blood was roughly proportional to the amount of the glycine ingested up to 3 grams. Increase beyond this amount did not cause a larger increase of the amino-acid in the blood. The increased amount of glycine (above 3 grams) does not appear in the urine, and it is assumed that it is fixed by the tissues. Analogous results were obtained in the case of dextrose. Similar experiments were carried out with alanine and leucine. An amount of leucine equivalent to 3 grams of glycine caused no increase in the amino-acid nitrogen in the blood, but a marked increase in the carbamide output in the urine. The conclusion is drawn that leucine is rapidly deamidised. Experiments were also carried out with mixtures of the above amino-acids and with silk-peptone, gelatin, Witte's peptone, egg-albumin, and peptonised egg-albumin. From the results the conclusion is drawn that these proteins, which yield on hydrolysis no glycine or only insignificant amounts of this substance, give rise to no increase in the amino-acid nitrogen of the blood when ingested *per os*, whereas those yielding relatively large amounts cause a corresponding increase, accompanied by an increased output of amino-acids in the urine. Attempts were made to explain the difference between the action of leucine and glycine as due to the differences in the permeability of the liver cells to these substances. Lobes of frog's liver, after being kept in isotonic Ringer solution, were transferred to a mixture of Ringer's fluid and isotonic solutions of these amino-acids. They were then put back into Ringer's fluid, and the changes of weight registered by a torsion balance. The results indicate that the glycine passes into the liver cells relatively rapidly, whereas leucine does not. It appears, therefore, that glycine passes into the blood because it does not, like leucine, become rapidly deamidised in the liver. S. B. S.

Nitrogenous Metabolism. Replacement of Food Proteins by the Mixture of Amino-acids prepared from them. Biological Values of Amino-acids prepared from Tissues of the Same Kind, and of a Different Kind of Animal. Biological Values of *l*-Tryptophan, *l*-Tyrosine, *l*-Phenylalanine and other Amino-acids. Replacement of *l*-Tyrosine and *l*-Phenylalanine by their Oxidation Products, Phenylpyruvic and *p*-Hydroxyphenylpyruvic Acids. Influence of Potassium Nitrate, Ammonium Salts, Urea, Sodium Acetate and Single Amino-acids on Nitrogenous Metabolism. The Utilisation of the Nitrogen of Ammonia and of Potassium Nitrate. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1915, **96**, 1—147).—The first part is devoted to a rigid experimental examination of the theory of the indispensability of certain of the amino-acids for the maintenance of nitrogenous equilibrium.

Directions are given for the preparation from proteins of mixtures of amino-acids by digestion with gastric juice and then with pancreatic and intestinal juices. Animals (dogs and rats) are then fed with one of these mixtures, and after nitrogenous equilibrium has been attained, a similar mixture is administered from which, however, one of the amino-acids has been removed. Such a mixture is prepared by removing one class of amino-acids by suitable treatment (for example, lysine, arginine, and histidine by precipitation with mercuric chloride), and then replacing the amino-acids other than the one the absence of which from the mixture is desired. If a negative nitrogenous balance is now obtained, the missing amino-acid is regarded as probably indispensable, and this conclusion is confirmed by adding the missing amino-acid and observing the re-establishment of nitrogenous equilibrium or a positive nitrogenous balance. In the case of tryptophan, the results confirm those of Hopkins and Willcock (A., 1907, ii, 109), who showed that this amino-acid is indispensable for the maintenance of life in mice. The removal of *l*-tyrosine from the amino-acid mixture is also accompanied by an immediate negative nitrogenous balance. The subsequent addition of either tyrosine or phenylalanine to the diet improves the balance, but actual nitrogenous equilibrium is not achieved. Apparently the animal organism requires a definite amount of homocyclic compound, which can be supplied by either tyrosine or phenylalanine.

The removal of lysine, arginine, or histidine destroys the life-maintaining capacity of the amino-acid mixture, but after the subsequent addition of the missing amino-acid the nitrogenous balance, although improved, is not restored to the original position. Similar experiments with proline, cystine, and glutamic acid gave inconclusive results. Attempts to replace tyrosine and phenylalanine with the corresponding oxidation products (*p*-hydroxyphenylpyruvic and phenylpyruvic acids) were unsuccessful, indicating the inability of the organism to synthesise the homocyclic amino-acids under the observed experimental conditions (compare Knoop, A., 1910, ii, 880).

In the second part of the communication the author gives the

results of further feeding experiments on dogs with nitrates and ammonium salts. Potassium nitrate is practically quantitatively recovered from the eliminated urine. During the period of its administration with the food, the excretion of the other, normal, nitrogenous products is slightly depressed. The ingestion of ammonium salts, urea, and also of sodium acetate is attended with similar results, and the author draws the conclusion that these substances do not take directly any part in nitrogenous metabolism (compare Grafe, A., 1913, i, 925).

The results of the experiments in which rats were fed with the products obtained by the total hydrolysis of rats on the one hand and the total hydrolysis of rabbits or dogs on the other were found to be dependent on the state of nutrition of the animals. If the rats are in a fasting condition, feeding with hydrolysed rats is accompanied by a larger positive nitrogenous balance and a correspondingly more rapid growth than can be obtained by feeding with the products of hydrolysis of an animal of a different species. In the case of well-fed rats, however, it does not matter whether the food originates from an animal of the same or of a different species —the nitrogenous products have apparently the same value.

H. W. B.

Newer Standpoints in the Study of Nutrition. FREDERICK GOWLAND HOPKINS (T., 1916, **109**, 629—649).—A lecture delivered before the Chemical Society. D. F. T.

Nutritive Deficiencies of Wheat and Grain Mixtures and the Pathological Conditions Produced in Swine by their Use. E. B. HART, W. S. MILLER, and E. V. MCCOLLUM (*J. Biol. Chem.*, 1916, **25**, 239—259).—The addition of a considerable proportion of wheat to the diet of swine appears to introduce a toxic factor which after the lapse of a few months induces histological changes in the nervous system resembling those occurring in cases of beriberi, and resulting in inhibited growth, followed by decline in body-weight and eventually in the death of the animal. The nerve degeneration caused by the absence of certain factors from the diet may thus be produced, apparently, by the presence of a toxic substance associated with the wheat grain. The toxic action is neutralised by supplementary materials, such as alfalfa (lucerne), commercial "meat scraps," milk, etc. Similar pathological conditions may also be produced if the salts in the food are either insufficient in quantity or lacking in variety. Striking photographs of the swine with accompanying sections of spinal cord, illustrating the changes produced by the various diets, are appended.

H. W. B.

Nutrition Investigations on Cotton-seed Meal. I. ANNA E. RICHARDSON and HELEN S. GREEN (*J. Biol. Chem.*, 1916, **25**, 307—318).—Feeding experiments on rats show that cotton-seed meal contains sufficient protein and fat-soluble growth-promoting substances, but not sufficient mineral matter for the growth and

maintenance of animal life. It is devoid of toxic properties. Cotton-seed meal has a greater nutritional value than cotton-seed flour.

When the diet is adequately augmented, rats grow and develop at the normal rate. On a diet containing 45% of cotton-seed flour, 17% of milk powder, 10% of starch, and 28% of lard, rats have grown and have borne one or more litters of young, which have, in their turn, exhibited normal growth on the same diet as the mothers. Some of the rats have lived for more than 345 days on a diet containing 50% of cotton-seed meal as the sole source of protein. H. W. B.

Are there Substances, at present unknown, which are of Importance for the Maintenance of Life? II. EMIL ABDERHALDEN and GOTTFRIED EWALD (*Chem. Zentr.*, 1916, i, 761—763; *Zeitsch. gesamte expt. Med.*, 1915, **5**, reprint 98 pp. Compare A., 1913, i, 1409).—Various further experiments on the feeding of pigeons on rice both with and without the husks are described, as the result of which the question of the existence of an essential, but still unknown, foodstuff is still undecided. It is regarded as certain that the alcoholic extract of rice bran (the so-called vitamine) in most cases relieves the disorders arising from an exclusive diet of husked rice. The introduction of methylglyoxaline into the diet induced in part phenomena of polyneuritis similar to those occasioned by the rice diet, but with the addition of vitamine, death was exceptional. On the other hand, the phenomena caused by β-amino-4-ethylglyoxaline were not influenced by vitamine. It seems improbable that only one specific "something" is present in the various complete foods. In consideration of the possibility of a known foodstuff being withheld by the removal of the husk from the rice, attempts were made, but without success, to influence the injurious effects by the addition of such substances as sodium or potassium chloride, sodium, lithium, or manganese carbonate, iron, calcium, or magnesium salts, etc. Atropine appeared to alleviate or even banish the disorders. G. F. M.

Is Autolysis an Autocatalytic Phenomenon? An Interpretation. H. C. BRADLEY (*J. Biol. Chem.*, 1916, **25**, 201—204. Compare Morse, this vol., i, 299).—The writer contends that unless the acids produced during autolysis arise through the direct agency of proteolytic enzymes, the process of autolysis should not be described as autocatalytic. He regards the acids produced during autolysis as altering the condition of the protein substratum, and thus affecting the rate of digestion by other means than by direct enzyme activation. H. W. B.

Autolysis. III. The Effect of Reaction on Liver Autolysis. H. C. BRADLEY and JOSEPH TAYLOR (*J. Biol. Chem.*, 1916, **25**, 261—280. Compare A., 1915, i, 1028).—The progressive addition of alkali, or of alkaline salts, to liver tissue reduces the rate and extent of liver autolysis in rough proportionality to the amount added until complete or nearly complete inhibition results. On the

other hand, the addition of acids or acid salts leads to a corresponding increase in the rate and extent of autolysis. These effects are believed to be due to changes occurring in the liver proteins, and not to activation or inhibition of the autolytic enzymes, because the digestion of foreign proteins such as caseinogen and gelatin added to the liver tissue is not affected in a similar manner by alterations in the concentration of hydrogen ions. Thus, autolysis of the liver may be almost completely inhibited by the addition of a salt which actually accelerates the digestion of caseinogen by the liver; acids, which hasten the autolytic process, do not alter the rate of digestion of caseinogen and peptone, etc. These results lead the authors to the hypothesis that the living cell contains two classes of proteins: (i) available, or capable of being acted on by the autolytic enzymes, and (ii) non-available or reserve proteins, and that the equilibrium between the two classes is dependent on the concentration of hydrogen ion in the cell at the moment. The non-available protein may be a protein salt or a polymerised protein aggregate, which, when an increase in the acidity occurs, may become dissociated or dispersed, and thereby transformed into a condition capable of combining with, and being broken down by, the autolytic enzymes into free amino-acids.

This hypothesis is applied for the explanation of certain conditions involving autolysis, or the reverse process of hypertrophy, in the living organism, such as acidosis, atropy induced by local tissue asphyxia, by embolism, or by ligation of arteries, phosphorus poisoning, etc. In these conditions, the autolysis is preceded by an accumulation of acid substances within the cell. H. W. B.

Protein Content of Muscle. N. W. JANNEY (*J. Biol. Chem.*, 1916, **25**, 185—188).—The proteins of muscle contain considerably more than 16% of nitrogen. It is not permissible, therefore, to estimate the quantity of protein in muscle by multiplying the total muscle nitrogen by the factor 6·25. As a matter of fact, the amount of protein thus calculated exceeds that estimated by actual analysis in the manner already described by the author (this vol., ii, 460) by about 15—20%.

The percentage of protein in muscle lies between the values 16·3 and 17·8 for animals of all species, even those as far separated zoologically as man and fish. H. W. B.

Protoplasmic Equilibrium. G. H. A. CLOWES (*J. Physical Chem.*, 1916, **20**, 407—451. Compare this vol., i, 349).—The influence of electrolytes on the nature and stability of oil–water emulsions has been examined, and the results compared with data which show the influence of the same electrolytes and their mixtures on living cells. By such a comparison, it was thought that it might be possible to explain the antagonistic electrolyte effects which appear to play an important part in cell life, and to throw some light on the structure of protoplasm and the mechanism of certain vital processes.

In regard to their influence on the equilibrium of oil–water

emulsions, electrolytes appear to be roughly divisible into two groups. The electrolytes in the one group promote the formation of emulsions of water in oil, and consist of salts of bi- and ter-valent cations. The electrolytes in the second group favour the formation of emulsions of oil in water, and include the alkali hydroxides and salts of univalent cations and bi- and ter-valent anions. Quantitative data expressing the influence of electrolytes were obtained by stalagmometric experiments, in which aqueous solutions of soap, containing the electrolytes under examination, were allowed to flow from a capillary pipette into olive oil, and the drop number determined. Electrolytes with a readily absorbed anion produce an increase in the drop number, indicating increased dispersion, destruction of the surface film, and an increased permeability of the oil to water. Electrolytes with a readily absorbed cation have the opposite effect. Sodium chloride increases the drop number, whilst calcium chloride reduces it. In solutions which contain sodium chloride and calcium chloride in the ratio of 50:1 or 100:1, the ratio depending on the absolute concentration, the antagonistic effects produced by the two salts are approximately balanced. These ratios are approximately the same as those in which the salts occur in sea-water, in the blood of mammals, etc., and equal to those in which their antagonistic effects are balanced according to various biological observations.

Salts of magnesium, which have been found to be anomalous in their biological effects in that they exert a protective or destructive effect on the protoplasmic film, according to the conditions, are found to exhibit similar anomalies in regard to their influence on the equilibrium of emulsions.

A comparison of the antagonism, which is exhibited by calcium chloride and sodium citrate in their influence on the equilibrium of emulsions, the coagulation of blood and the hæmolysis of blood corpuscles, has shown that the ratio of the concentrations, at which their effects are mutually compensated, is approximately the same in all cases.

Similar relations between the effects produced in physical and biological systems have been found in experiments with anæsthetic substances. The concentrations at which these exert maximum protective effects on emulsions correspond closely with those at which they exert similar protective effects on living cells.

There is consequently strong evidence for the view that the antagonistic effects produced by the two groups of electrolytes, which have been referred to above, in biological systems are closely parallel and presumably of the same nature as the antagonistic effects which appear to have been established by observations on purely physical systems. H. M. D.

Bence-Jones Proteinuria. A. E. TAYLOR and C. W. MILLER (*J. Biol. Chem.*, 1916, **25**, 281—295).—The authors have studied the properties of the protein in the urine in a case of Bence-Jones proteinuria.

When the Bence-Jones protein is heated with a small amount of

acetic acid, its coagulation temperature is raised, but on boiling it redissolves in the characteristic manner, and is reprecipitated on cooling. Saturation of the urine with most salts only partly precipitates the protein, but if excess of acid is also added, the precipitation is complete.

To distinguish between normal serum and Bence-Jones protein, a drop of concentrated nitric acid is added to a few c.c. of the urine in a test-tube. A white precipitate is formed, which disappears on shaking. More drops of the acid are then added, shaking between each addition, until the precipitate no longer dissolves. Now one or two drops more of the acid are added, and the contents of the tube heated to boiling. If the precipitate is Bence-Jones protein, it quickly dissolves and reappears on cooling; if, on the other hand, the precipitate is due to normal serum protein, it does not dissolve on boiling but becomes of a yellow or brown colour. If the first drop of nitric acid produces a thick, curdy precipitate, the urine should be diluted before performing the test. In some cases the Bence-Jones protein is accompanied by a small amount of serum protein.

The Bence-Jones protein is readily separated from the urine by saturation with sodium sulphate in the presence of excess of acetic acid. After subcutaneous injection of the urine, or of the separated protein dissolved in Ringer's solution, into guinea-pigs, the animals become sensitised and show marked anaphylaxis when an intravenous injection is subsequently made. Direct intravenous injection of as much as 2 grams per kilo. of the protein dissolved in slightly alkaline Ringer's solution is not followed by any toxic effects. The substance is therefore not of a proteose nature, but is more closely allied to the normal proteins of the blood.

H. W. B.

Tetany of Parathyroidectomised Dogs. ISIDOR GREENWALD (*J. Biol. Chem.*, 1916, **25**, 223—226).—If the diminished excretion of phosphorus previously noticed to occur after parathyroidectomy in dogs (A., 1911, ii, 507) is due to its retention as phosphate, the phosphate cannot be the cause of the tetany owing to its well-established non-toxic properties. Other phosphorus compounds have been examined with regard to their toxicity in dogs, and particularly inosic acid present in muscular tissue. After injection intravenously into a dog, from which the thyroid and parathyroids had been previously removed, a toxic effect was not observed; and in the serum of parathyroidectomised dogs in which tetany was just developing, the hydrolytic products of inosic acid were absent. The hypothesis that inosic acid is the toxic agent in the causation of the tetany of parathyroidectomised dogs is therefore abandoned, and the significance of the retention of phosphorus remains unexplained.

H. W. B.

Action of some Porphyrins on Paramœcia. HANS FISCHER and G. A. VON KEMNITZ (*Zeitsch. physiol. Chem.*, 1915, **96**, 309—313).—Mesoporphyrin has a stronger sensitising action on

paramœcia than hæmatoporphyrin. Urinoporphyrin and coto-porphyrin do not produce any visible effects. H. W. B.

The Appearance of Hæmatin in Blood after Poisoning with Chlorates. JOH. FEIGL (*Biochem. Zeitsch.*, 1916, **74**, 394—413).—The presence of hæmatin in the blood was confirmed in the case of a hospital patient, and also in the cases of animals (chiefly cats) to which chlorates had been administered. In some cases large doses were given, so as to produce death within two to ten hours; in others smaller doses were given, producing death within ten to twenty-four hours; and in others, again, sub-acute intoxication was produced lasting up to two weeks. In both acute and mild intoxications hæmatin could be detected. A short account of other symptoms of chlorate poisoning is also given. S. B. S.

The Oligodynamic Action of Copper. The Nature of Antagonism. K. SPIRO (*Biochem. Zeitsch.*, 1916, **74**, 265—274).—The author distinguishes between true antagonism (ion antagonism), where one substance acts directly on another, and apparent or "pseudo-antagonism," where one substance replaces another in its action on a third substance.

He attempts to determine the nature of the antagonistic action of various salts to the toxic action of copper, such as is known to occur when water distilled in copper stills is used in various biological experiments. As regards the action of various anions, it is shown that they can be divided into three groups, namely, those which reduce cupric salts to cuprous salts (KNCS, I, CN), the halogen ions, which form oxyhalogenoids, and a third group, which form complex salts. The solvent action of solutions of various salts on copper was investigated, and the results were those to be expected from the various actions of the anions, and the influence of these salts on the oligodynamic action of copper was found to run parallel with the solubility of the metal in their solutions. The conclusion was drawn that there is no direct antagonism between copper and sodium, but that the influence of sodium salts on the oligodynamic action depends on the anions. S. B. S.

Relative Toxicity of Substances Found in Foods. ALFRED N. COOK and SYLVANNA ELLIOTT (*J. Ind. Eng. Chem.*, 1916, **8**, 503—504).—Results of the action of various substances on frogs and fishes are recorded. Sucrose, potassium sodium tartrate, dextrose, alcohol, and potassium oxalate were all less toxic to fishes than was sodium benzoate. In the case of frogs, however, all these substances were more toxic than sodium benzoate. Citric, acetic, malic, and tartaric acids were more toxic than caffeine or "saccharin" to fishes, whilst citric and malic acids were less toxic than "saccharin" to frogs. These organic acids were even more toxic than phenol to fishes, whereas the reverse held true in the case of frogs. With both fishes and frogs, alum was more harmful than was either sodium benzoate or "saccharin." The various effects of many other substances are also given, but the

authors conclude that experiments of this nature, at least on animals so distantly related to man, do not furnish conclusive evidence of the effects of the substances on the human system.

W. P. S.

The Toxicity, Resorption, and Excretion of Cotoin and similar Substances, and of Paracotoin. A. IODLBAUER and S. KURZ (*Biochem. Zeitsch.*, 1916, **74**, 340—356).—Cotoin and the allied substances alizarin-yellow *A*, hydrocotoin, and fortoin are not general protoplasmic poisons, and can be tolerated in fairly high concentrations by infusoria. By employment of fish and tadpoles, the relative toxicity was investigated. This increases from alizarin-yellow *A* (without a methyl group) to cotoin (with one methyl group), to hydrocotoin (with two methyl groups), which is the most toxic. The conjugation of two cotoin groups with a methyl group (fortoin) increases its toxicity. The voluntary movements of fish and tadpoles are stopped before the respiration, and in suitable concentration the former are restored after a certain interval. The stoppage appears, from the observations made on frogs, to be due to an action on the central nervous system. Paracotoin, although chemically different, acts in a similar manner to the above-mentioned substances. All are very slightly toxic to warm-blooded animals. Cotoin and allied substances are resorbed from the intestine and are excreted completely in the urine, conjugated either as sulphates or as glycuronates.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Mechanism of Fermentation. A. FERNBACH (*J. Inst. Brewing*, 1916, **22**, 354—367).—In presence of calcium carbonate, fermentation is slightly retarded for a day or two; by the fourth day the amount of sugar is about the same with or without calcium carbonate, whilst subsequently there is increased activity under the influence of calcium carbonate. After the second day there is a great increase in the production of acids in the solutions containing calcium carbonate, about five times as much acid being produced under these conditions as in the absence of calcium carbonate.

The chief acid formed in the fermentation process was found to be pyruvic acid, which is readily converted into carbon dioxide, and acetaldehyde, which is reduced to alcohol. The small amounts of acetaldehyde found in fermented liquids are therefore residues which the yeast has failed to reduce to alcohol, and not the result of the oxidation of alcohol.

It is suggested that succinic acid may be formed by the condensation of 2 mols. of pyruvic acid and the transformation of the

lactone into pyrotartaric (methylsuccinic) acid, which should yield succinic more readily than hydroxyglutaric acid, as suggested by Ehrlich.

In addition to pyruvic acid, certain amounts of succinic, acetic, and lactic acids were found. N. H. J. M.

Digestion of Cellulose. W. ELLENBERGER, A. SCHEUNERT, W. GRIMMER, and A. HOPFFE (*Zeitsch. physiol. Chem.*, 1915, **96**, 236—254).—A fungus has been discovered which digests cellulose. It is present in the soil, in cheese, in the stomach, cæcum, and colon of the horse, the pig and the ox, in straw, and in the fæces of man and other animals. It flourishes in a culture medium containing cellulose in the form of filter-paper, straw, hay, dried cabbage, or ordinary writing-paper. It continues to grow for some days in the absence of nitrogen, but quickly forms spores unless a nitrogenous substance is added to the culture medium.

Other carbon compounds may be substituted for the cellulose in the above experiments. Mannitol and ordinary alcohol constitute excellent sources for the carbon required by the fungus, which is extraordinarily immune to the action of strong alcoholic solutions. The fungus continues to grow in 80% alcohol, and 96% alcohol does not destroy the spores. The activity of the fungus is slightly diminished in the presence of 0·5% hydrochloric acid and ordinary gastric juice, but is not completely inhibited; and when the fungus is transferred to a fresh culture medium containing cellulose it digests the latter at the original rate.

The enzyme responsible for digesting the cellulose has been isolated by growing the fungus for some time in a culture medium containing cellulose, and then filtering through a Berkefeld filter. The filtrate is free from cells and retains its power of dissolving cellulose for several weeks. The nature of the products obtained from cellulose under the action of this enzyme has not been established. H. W. B.

Nutrition of Green Plants by means of Organic Compounds. I. CIRO RAVENNA (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 649—655).—Experiments have been made on the growth of maize under sterile conditions in solutions containing inorganic salts, together with different proportions of dextrose. The leaves of the plants thus developed are found to contain starch even although access of carbon dioxide is excluded, but exposure to light is indispensable. The region of the solar spectrum, which has the greatest influence on the formation of starch under such conditions, is that which exerts the maximum effect on the functions of chlorophyll. In absence of oxygen as well as of carbon dioxide, plants grown in sugar solutions do not form starch in the leaves even in the light. These results are regarded as evidence supporting the author's hypothesis, according to which sugar absorbed by the roots is oxidised in the interior of the plant by atmospheric oxygen to form carbon dioxide, the latter being converted into starch by the chlorophyll in the leaves. T. H. P.

Action of Manganese Salts on Vegetation. GIULIO MASONI (*Chem. Zentr.*, 1916, i, 299; from *Staz. sperim. agrar. ital.*, 1915, **48**, 822—838. Compare A., 1911, ii, 821).—The addition of manganese chloride and sulphate to soils appeared to increase the growth of plants, but to so small an extent that it was impossible to assign any specific action to the salts. W. P. S.

Urease Content of Certain Beans, with Special Reference to the Jack Bean. J. G. MATEER and E. K. MARSHALL, Jr. (*J. Biol. Chem.*, 1916, 297—305).—Different varieties of beans contain very different amounts of urease. The jack bean (*Canavalia ensiformis*) contains more than fifteen times, and the sword bean (*C. gladiata*) about five times as much urease as the soja bean, whilst *Dolichos biflorus* contains about one-fifth, the white lupin about one-fiftieth, *Phaseolus aureus* about 1/350th of the amount of urease contained in the soja bean. The urease of the jack bean, like that of the soja bean, is specific, acting only on urea; the aqueous extract of the bean does not decompose erepton, caseinogen, hippuric acid, creatinine, tyrosine, or other amino-acids, uric acid, adenine, or guanine.

For most purposes the urease is extracted from the ground bean by keeping it in contact with ten times its weight of water for an hour. On centrifugalising, a clear extract is obtained. The enzyme may be obtained in solid form by precipitation of the aqueous extract with acetone. H. W. B.

The Galactan of Larix Occidentalis. A. W. SCHORGER and D. F. SMITH (*J. Ind. Eng. Chem.*, 1916, **8**, 494—499).—The wood of the western larch, *Larix occidentalis*, yields from 8 to 17% of water-soluble substance, which consists almost entirely of a galactan, the average quantity of the latter being 10%. This galactan decomposes at 250°, has $[\alpha]_D^{20}$ +12·11°, and yields only galactose on hydrolysis; it is ϵ-galactan. Galactans are characteristic of the Coniferæ. The estimation of galactans by oxidation to mucic acid according to Tollen's method was found to be untrustworthy. W. P. S.

The Behaviour of the Cell Nucleus towards Different Poisons. OSCAR LOEW (*Biochem. Zeitsch.*, 1916, **74**, 376—386).—At death, the nucleus of *Spirogyra* can contract in two ways, either spherically or laterally. The spherical contraction is the more usual form of change, and the second form of change is produced more especially by salts which precipitate calcium, such as potassium oxalate and sodium fluoride. Other salts which precipitate calcium exert a similar action, but they produce the effect more slowly and in higher concentrations; included in these are dipotassium orthophosphate, dipotassium carbonate, and tripotassium citrate. Sodium pyrophosphate and metaphosphate, on the other hand, act as strongly as the oxalate.

Potassium sulphate and dipotassium tartrate remain in 0·5% solution for a long time without action. Acid salts and acids produce the spherical contraction. The toxic action of magnesium

salts is ascribed to their replacement of calcium. Calcium salts inhibit the toxic action of magnesium salts. Cells remain an indefinite time in a living state in the presence of calcium salts when other salts are absent. S. B. S.

Pentose and the So-called Furfuroids. EDUARD KUNZ (*Biochem. Zeitsch.*, 1916, **74**, 312—339).—The chaff investigated contains two kinds of substances which yield furfuraldehyde, one of which can be readily hydrolysed, whereas the other cannot. An approximate separation of the two can be accomplished by heating for several hours with 2% sulphuric acid. The substance, which is rendered soluble by this treatment, is arabinose, and the parent-substance must therefore be regarded as a genuine pentosan. The residue is very resistant to the action of dilute acids, and can be best degraded by the action of 1% sulphuric acid under the pressure of 3—4 atmospheres. Under these conditions about 90% of the residue is rendered soluble. Various reactions indicate that the dissolved substance in this case is also arabinose, and the mother substance some kind of a pentosan. The conclusion is drawn that substances described as furfuroids, contrary to what has sometimes been suggested, probably also contain a pentosan complex; there is no evidence, according to the author, that they contain a methylene ether complex. S. B. S.

Influence of Calcium Carbonate on Maize. A. W. BLAIR and H. C. McLEAN (*Soil Sci.*, 1916, **1**, 489—504).—The results of plot experiments in which ground limestone was applied to a medium loam soil at the rate of 2 tons per acre showed an increase of about 10 bushels of grain. The effect of limestone when applied to plots which had ammonium sulphate was especially marked, and applications of limestone in conjunction with nitrogen in the form of wheat or rye straw were also found to increase the yields.

The percentage of nitrogen in the crop was slightly increased by limestone, whilst the average recovery of nitrogen was increased from 25% on the unlimed plots to 36·2%. N. H. J. M.

Toxic Action of Soluble Aluminium Salts on the Growth of the Rice Plant. K. MIYAKE (*J. Biol. Chem.*, 1916, **25**, 23—28).—Aluminium chloride inhibits the growth of rice seedlings in solutions of concentration greater than $N/7500$. The toxicity appears to be due to the aluminium ions, and not to the hydrogen ions liberated by the partial hydrolysis of the aluminium chloride occurring in dilute aqueous solutions. H. W. B.

Nature of the Injurious Action of Sulphur on Plants and the Foundations of Buildings. WILHELM THÖRNER (*Zeitsch.-angew. Chem.*, 1916, **29**, i, 233—236).—The sulphur present in peat as ferrous sulphide, free sulphur, and as organic compounds is harmless when below the water table. When, however, the peat soil is worked, or the water table lowered, the oxidation of the ferrous sulphide to ferrous sulphate and sulphuric acid is fairly rapid, and free sulphur is also oxidised. The oxidation products are not only injurious to plants, but also to mortar and cements.

Finely divided sulphur distributed in sand and in peat is slowly oxidised, probably by ozone, hydrogen peroxide, and nitrous acid.

N. H. J. M.

The Oxidising Power of Soil in Connexion with Aeration. F. C. GERRETSEN (*Chem. Zentr.*, 1916, i, 678; from *Mededeelingen Proefstation Java-Seukerindustrie*, 1915, **5**, 317—331).—Soils show distinct differences in oxidising power towards hydrogen iodide; those not giving the reaction at all contain generally ferrous iron. The iron compounds and organic matter play an important part in the reduction. It is probable that oxydases are also present. The sugar-cane was not in a good condition in soils which did not liberate iodine from hydrogen iodide. The hydrogen iodide number indicates the condition of a soil provided that a sufficient quantity of iron compounds soluble in dilute sulphuric acid is present. A reduced soil readily absorbs oxygen, and in many soils a connexion can be traced between the degree of aeration and the hydrogen iodide number.

G. F. M.

Cause and Nature of Soil Acidity with Special Regard to Colloids and Adsorption. E. TRUOG (*J. Physical Chem.*, 1916, **20**, 457—484).—A critical review of the work which has been done, and the theories which have been propounded to explain the cause and nature of soil acidity. The selective ion adsorption theory and the mineral acid theory are considered in detail in connexion with the experimental data on which they are based. It is shown that in adsorption the molecules as a whole are concentrated at surfaces. A certain substance may be adsorbed more than others, depending on conditions, and this is designated selective adsorption. The existence of selective adsorption of ions from the common alkali and alkaline-earth salts is questionable. The phenomenon observed with these salts is small in extent, and commensurate with chemical reactions that might be expected of impurities in the adsorbent. The phenomenon observed in acid soils and often designated as selective adsorption of ions is of entirely higher order in extent, and comparable in every way with chemical reactions between acids and bases. The failure of investigators to demonstrate that acid soils take up chemically equivalent amounts of different bases has been the one strong argument against the existence of true acids as the cause of soil acidity. This argument no longer holds, since it is shown in the present paper that, when the conditions are properly controlled, it can be demonstrated that the reactions due to soil acidity take place according to chemical equivalence, and exhibit all the properties of true chemical reactions. The possibilities for the formation of true acid substances in soils of humid regions are manifold, and it would be extremely difficult to explain why such substances should not be formed. In most upland soils mineral acids, such as kaolinite and other acid silicates, are the main causes of soil acidity. Soils rich in organic matter may contain considerable amounts of organic acids. These acid substances may be either in the crystalline or colloidal condition, and the acid reaction is due to their chemical nature, and not to their colloidal condition.

J. F. S.

Decomposition of Cellulose in Soils. I. G. McBeth (*Soil Sci.*, 1916, **1**, 437—487).—Twenty-five species of cellulose-dissolving bacteria were grown on media containing cellulose prepared from lucerne flour, and all were found to dissolve the cellulose as readily as that prepared from filter paper. The organisms develop most readily in air; some growth can, however, be obtained under anærobic conditions. Whilst most of them grow well on ordinary culture media, a few grow only in presence of cellulose. The organisms assimilate nitrogen both in inorganic and organic forms, peptone being the most favourable for the largest number of species, and casein usually the least favourable.

With dextrose, lactose, maltose, sucrose, and starch the amount of acid formed in twelve days at 30° is usually between 1 and 2% on Fuller's scale; in mannitol and glycerol solutions the acidity is usually less than 1%, and in some cases no acid is formed at all.

For estimating the nitrate-reducing power of the organisms, a starch-nitrate solution was employed, as it was found that many species produce small amounts of nitrite in Dunham's solution, presumably from the peptone.

Filamentous fungi are of greater importance in the destruction of cellulose in the humid soils in the east of the United States than in the semi-arid soils of Southern California. In the latter soils the rapid destruction of cellulose is probably due to favourable conditions of climate and cultivation rather than to the specially active nature of the soil flora. N. H. J. M.

Atmospheric Pollution. First Report of the Committee for the Investigation of Atmospheric Pollution (*Lancet*, Feb. 26th, 1916, **190**, Suppl., 40 pp.).—Analyses of monthly samples of rain-water collected at seven places in the County of London and at forty places in eighteen towns in England and Scotland during the year ending March, 1914. In many cases the results extend over the whole year. The results include insoluble matter (tar, carbonaceous other than tar and ash), soluble matter (loss on ignition and ash), total solids, sulphates, chlorides, and ammonia, and are expressed in metric tons per sq. kilometre.

The amounts of total solids per month varied from 20·5 kilos per hectare at Malvern to 347·0 kilos at Oldham, whilst the tar varied from 0·0 to 3·7 kilos at the same places. Soluble ash amounted to 10·3 kilos at Malvern and 96·4 kilos at Bolton (the highest). Sulphates (SO_3) were lowest at Malvern (4·4 kilos) and highest at Bolton (46·2 kilos per hectare), whilst the lowest and the highest amounts of chlorides were obtained at Coatbridge (2·7) and at Bolton (20·2 kilos per hectare). Nitrogen, as ammonia, varied from 0·08 kilo at Malvern to 4·7 kilos in Liverpool.

As regards the influence of seasons it is shown that the highest results for total solids, soluble ash, sulphates, and chlorides are obtained in the winter months. Insoluble ash was highest in spring, whilst ammonia was highest in summer.

The samples were all collected in a standard gauge, described with sketch, and maps (1 inch to a mile) are given for each district showing the positions of the gauges. N. H. J. M.

Organic Chemistry.

Action of Anhydrous Aluminium Chloride on Unsaturated Compounds. W. E. HENDERSON and WILMER C. GANGLOFF (*J. Amer. Chem. Soc.*, 1916, **38**, 1382—1384).—It is well known that aluminium chloride combines with unsaturated hydrocarbons, but hitherto no well-defined products have been recorded. A study of these reactions has therefore been undertaken, and the following results have already been obtained.

Baud (A., 1900, i, 369) found that when acetylene was passed over heated aluminium chloride, certain products were obtained, to which he assigned the formulæ $7C_{20}H_{15},Al_2Cl_6$ and $7C_{10}H_{15},Al_2Cl_6$. This work has now been repeated, and a black sublimate was obtained, which was evidently a complex mixture.

When an alcoholic solution of aluminium chloride is saturated with acetylene and left for about five days, small, lustrous crystals separate which are hygroscopic and very unstable, and appear to have the composition $AlCl_3,2C_2H_2,2H_2O$.

Ethylene yields a similar crystalline compound, which probably has the composition $AlCl_3,3C_2H_4,H_2O$. Crystalline products have also been obtained with propylene, butylene, styrene, oleic acid, and amylene. E. G.

Hydrolysis of Chloropentanes as Affected by High Pressure. Synthetic Fusel Oil. HARRY ESSEX, HAROLD HIBBERT, and BENJAMIN T. BROOKS (*J. Amer. Chem. Soc.*, 1916, **38**, 1368—1374).—Meyer and Bergius (A., 1915, i, 231) have shown that chlorobenzene can be converted, first into phenyl ether, and finally into phenol, by heating it under pressure with sodium hydroxide solution of 15—20% strength, whilst it is but little affected by treatment, under the same conditions, with dilute alkali hydroxide, or with solutions of calcium hydroxide, sodium carbonate, or borax.

An account is given of similar experiments with a mixture of α-, β-, and γ-chloropentanes. It was found that the same yields of amyl alcohol were obtained with sodium carbonate as with sodium hydroxide, and even larger yields with sodium acetate under similar conditions. The amount of amyl ether obtained was small, and in no case exceeded 8%. The presence of cuprous chloride or basic lead carbonate had no influence on the rate or character of the reaction. When glacial acetic acid was used as the solvent, amyl acetate was obtained in much larger yields and at much lower pressures. When chloropentane was heated with water-vapour at atmospheric pressure until decomposition occurred, amylene was produced almost exclusively. E. G.

Some Complex Compounds of the Sugar Alcohols. ADOLF GRÜN [with I. HUSMANN and H. NOSSOWITSCH] (*Monatsh.*, 1916, **37**, 205—218).—In earlier papers (A., 1908, i, 934; 1910, i, 352)

the author described complex compounds of $\alpha\beta$-glycols and glycerols with metallic salts. The investigation has now been extended to the tetritols, pentitols, and hexitols.

A concentrated solution of erythritol gradually dissolves barium hydroxide on evaporation in a desiccator, forming *trierythritol barium hydroxide*, $[Ba{::::}3C_4H_{10}O_4](OH)_2$, as a hygroscopic powder, which reacts alkaline and absorbs carbon dioxide.

Similarly, mannitol forms *dimannitol barium hydroxide*,

$$2C_6H_{14}O_6,Ba(OH)_2,8H_2O;$$

dimannitol strontium hydroxide, $2C_6H_{14}O_6,Sr(OH)_2,8H_2O$; and a *compound*, $3C_6H_{14}O_6,2Ca(OH)_2$. *Di-dulcitol barium hydroxide*, $2C_6H_{14}O_6,Ba(OH)_2,8H_2O$, is a very similar substance.

As these complexes give colourless solutions, it is possible to employ polarimetric methods in the study of their constitution. It has been found that the alkaline-earth hydroxides enhance the activity of mannitol solutions. The above complexes are, therefore, not dissociated completely in solution, but the indication is that mono-mannitol complexes with still greater optical activity and free mannitol are the scission products. Strange to say, solutions of mannitol are rendered inactive by the addition of barium chloride, or calcium, strontium, or barium nitrate, which suggests the formation of complexes in these cases, but the matter has not been studied further. J. C. W.

Interaction of Hydroxy- and Amino-acids with Nitrophenylhydrazine, with Special Reference to the Formation of Glyoxal Derivatives. HENRY DRYSDALE DAKIN (*Biochem. J.*, 1916, **10**, 313—318).—Three products of the interaction of *p*-nitrophenylhydrazine and lactic acid have already been described (Dakin and Dudley, A., 1913, i, 925), namely (i) methylglyoxal-bis-nitrophenylhydrazone, (ii) α-nitrophenylhydrazinopropionic acid, and (iii) pyruvic acid nitrophenylhydrazone. A fourth product has now been discovered, the p-*nitrophenylhydrazide* of lactic acid, $OH\cdot CHMe\cdot CO\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2$, which is formed in relatively large amount. Similar crystalline derivatives have been prepared from *d*-lactic acid and from glycollic acid, whilst α-hydroxybutyric acid and β-hydroxybutyric acid gave only oily products.

Glycollyl-p-*nitrophenylhydrazide*,

$$OH\cdot CH_2\cdot CO\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2,$$

is prepared by warming a mixture of glycollic acid and *p*-nitrophenylhydrazine in aqueous alcohol. After extraction of unchanged *p*-nitrophenylhydrazine with chloroform, the hydrazide is extracted with amyl alcohol. The substance crystallises from boiling alcohol in lemon-yellow needles, m. p. 192—194°. It is readily soluble in water, and easily hydrolysed on boiling with acids.

i-*Lactyl*-p-*nitrophenylhydrazide* is similarly prepared. It is an almost colourless substance, and crystallises from alcohol in prisms and plates, which sinter at 162° and melt at 165—167°. d-*Lactyl*-p-*nitrophenylhydrazide* crystallises in prisms, m. p. 161—163°, $[\alpha]_D^{17^\circ} - 34{\cdot}5^\circ$.

A number of experiments have been performed to discover the

conditions which determine the variations in the relative yields of these four products. It appears that if the lactic acid is completely neutralised with sodium hydroxide before digestion with nitrophenylhydrazine, methylglyoxal bis-nitrophenylhydrazone is not formed. A free carboxyl group is apparently necessary for methylglyoxal formation. The addition of small amounts of a mineral acid inhibits the formation of phenylhydrazide and of methylglyoxal derivative, whilst the yield of hydrazino-acid is not materially affected. A low concentration of lactic acid favours the formation of methylglyoxal derivative and hydrazino-acid, whilst higher concentrations favour hydrazide formation. Formation of methylglyoxal-bis-nitrophenylhydrazone is not conditioned by the prior formation of lactylnitrophenylhydrazide, because the latter substance could not be converted into the former.

A number of hydroxy-acids have been tested with regard to their power of yielding glyoxal derivatives when treated with nitrophenylhydrazine. The production of a clear blue colour when tested with sodium hydroxide and alcohol was taken as evidence of the presence of a bis-nitrophenylhydrazone and probable indication of glyoxal formation. Positive results were obtained in the case of tartaric, gluconic, diethylglycollic, α-hydroxy*iso*butyric, and α-hydroxybutyric acids.

An attempt to replace nitrophenylhydrazine by semicarbazide in the reaction leading to the production of *iso*butylglyoxal from leucine was unsuccessful. Whether this is due to a too great solubility of the semicarbazone or whether glyoxal formation is in some way conditioned by the presence of nitrophenylhydrazine was not ascertained. H. W. B.

New Complex Compounds of Tervalent Vanadium. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 723—730).—The action of barium formate on tervalent vanadium sulphate yields a tervalent vanadium, basic formate, in which the ratio V : C has the value 1 : 2·4. This basic compound differs in behaviour from other basic compounds, since it crystallises in green needles, dissolves in methyl alcohol, and can be obtained of constant composition from solutions strongly acidified with formic acid. It appears to be analogous to Weinland and Reihlen's basic ferric formate (A., 1913, i, 1300), and in this case would have the formula:

$$[V(H\cdot CO_2)_6]\left[V_3{(H\cdot CO_2)_6 \atop (OH)_2}\right]_3,12H_2O \quad (I).$$

Sodium vanadiformate, $Na_3V(HCO_2)_6$, prepared either by dissolving the preceding compound in a hot, almost saturated sodium formate solution or by addition of excess of sodium formate to concentrated vanadium trisulphate solution, forms transparent, blue scales resembling the green crystals of sodium ferriformate (*loc. cit.*). The intermediate compounds,

$$[V(H\cdot CO_2)_6]\left[\left(V_3{(H\cdot CO_2)_6 \atop (OH)_2}\right)_2 Na\right] \quad \text{and}$$

$$[V(H\cdot CO_2)_6]\left[\left(V_3{(H\cdot CO_2)_6 \atop (OH)_3}\right)Na_2\right],$$

should also exist, but only what are probably mixtures of them could be obtained.

The *vanadium ammonium formate*,

$$[V(HCO_2)_6]\left[\left(V_3\begin{matrix}(HCO_2)_6\\(OH)_2\end{matrix}\right)(NH_4)_2\right],$$

was obtained pure in greyish-green needles.

Examination of the compound to which Belloni (A., 1909, i, 283) ascribes the constitution $HCO_2\left[Fe_3\begin{matrix}(HCO_2)_6\\(OH)_2\end{matrix}\right]4H_2O$, shows that the ratio Fe:C is 1:2·4, and not 1:2·33, the analytical results agreeing better with the formula $Fe_5(HCO_2)_{12}(OH)_3,14H_2O$ than with that given above; the conclusion is drawn that Belloni's compound is identical with that of Weinland and Reihlen (*loc. cit.*).

The action of water, especially in the hot, on compound I (vide supra) or on sodium vanadiformate results in the elimination of one of the six formyl radicles of the complex cation, with formation of the *compound*, $\left[V_3\begin{matrix}(HCO_2)_5\\(OH)_3\end{matrix}\right]HCO_2,2H_2O$, as an almost white, microcrystalline powder insoluble in water or alcohol. A similar change accompanies the action of water on basic chromic acetate (compare Weinland and Büttner, A., 1912, i, 530).

T. H. P.

Biochemical Synthesis of a Galactobiose. ÉM. BOURQUELOT and A. AUBRY (*Compt. rend.*, 1916, **163**, 60—62. Compare A., 1913, i, 1305).—By the action of emulsin on a concentrated aqueous solution of galactose, the authors have prepared a *galactobiose*, which could not, however, be obtained in a crystalline state. It has $[\alpha]_D^{19}$ +54·1° (in water); +39·3° (in 90% alcohol); and +49·18° (in 40% alcohol). It is hydrolysed in aqueous solution by emulsin or dilute sulphuric acid, galactose being re-formed. It gives an *osazone*, which is soluble in boiling water, and has m. p. 126·7° (corr.), thus differing from the osazone of the galactobiose described by Fischer and Armstrong (compare A., 1902, i, 746). The biose has a reducing power equal to 60·4% of that of the original galactose.

W. G.

The Configuration of α-Galactose and α-Fructose. J. BÖESEKEN, A. H. KERSTJENS, and C. E. KLAMER (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1654—1659).—Measurements have been made of the rate of change of the rotation of solutions of α-galactose in pure water and in 0·5 molar boric acid solution, and also of the rate of change of the conductivity of the boric acid solution. The results show that the mutarotation is only very slightly affected by the presence of boric acid. When the rotation and conductivity data are substituted in the equation for the unimolecular reversible reaction, both lead to the same constant. Although the influence of the galactoses on the conductivity of boric acid is very small, that of α-galactose is the greater, and this is supposed to be in favour of the *cis*-formula for α-galactose.

In the case of the fructoses, a very considerable increase in the

conductivity is found when these are added to a boric acid solution. Measurements of the rate of change of the rotation and of the conductivity of boric acid solutions of α-fructose at 0° gave the same constant, when the data were substituted in the velocity equation for a unimolecular reversible reaction. In agreement with the large increase in the conductivity on the addition of fructose to boric acid, this constant is much greater than that obtained from the data for the muta-rotation in pure aqueous solution. The fact that the conductivity increases as the transformation $\alpha \longrightarrow \beta$ fructose proceeds, indicates that the distribution of the hydroxyl groups is less favourable to complex formation in the case of the α-form, and this affords a means of determining the formula to be assigned to the two isomerides. H. M. D.

Synthesis of Humin Substances by the Action of Amino-acids on Reducing Sugars. L. C. Maillard (*Ann. Chim.*, 1916, [ix], **5**, 258—317).—A more detailed account of work already published (compare A., 1912, i, 169; 1913, i, 165, 595). W. G.

Isomeric Penta-acetates of Glucosamine and of Chondrosamine. C. S. Hudson and J. K. Dale (*J. Amer. Chem. Soc.*, 1916, **38**, 1431—1436).—Two isomeric penta-acetyl derivatives of glucosamine have been described by Lobry de Bruyn and Alberda van Ekenstein (A., 1899, i, 732). If these compounds are the corresponding α- and β-forms, then in accordance with the view expressed in an earlier paper (A., 1915, i, 501) the difference between their molecular rotations should be the quantity 2A (A representing the rotation due to the end asymmetric carbon atom), which has the same value for all acetylated aldoses. Lobry de Bruyn and Alberda van Ekenstein found the more soluble penta-acetate to have $[\alpha]_D$ +86·5°, and the less soluble form to be optically inactive, the molecular rotation difference thus being +33,600, whereas in the case of the dextrose penta-acetates the difference is +38,100. The glucosamine penta-acetates have therefore been prepared and purified, and their specific rotations re-determined, with the result that the α-form gave $[\alpha]_D^{20}$ +93·2° and the β-form $[\alpha]_D^{20}$ +1·2°. These values correspond with a molecular rotation difference of +35,800.

Levene and La Forge (A., 1915, i, 601) have prepared a chondrosamine hydrochloride, which is isomeric with glucosamine hydrochloride. Isomeric chondrosamine penta-acetates have now been prepared. The *α-penta-acetate* does not melt, but begins to darken at 220°, and is completely decomposed at 235°; it has $[\alpha]_D^{20}$ +10·5°. The *β-penta-acetate*, m. p. 182—183° (corr.), obtained by the action of acetic anhydride and a little zinc chloride on the α-form, has $[\alpha]_D^{20}$ +101·3°. The molecular rotation difference in this case is therefore −35,400, which agrees closely with the value 35,800 observed in the case of the glucosamine penta-acetates. These values, however, do not agree very well with that obtained for the dextrose penta-acetates, the divergence amounting to about 6° in specific rotation in one case, and 7·5° in the other. This indicates that the nature of the groups in the chain has a small influence on the rotation of the end asymmetric carbon atom. E. G.

Oxidation of Amino-acids to Cyanides. HENRY DRYSDALE DAKIN (*Biochem. J.*, 1916, **10**, 319—323).—When excess of sodium *p*-toluenesulphochloroamide acts on an amino-acid, cyanides are produced with the probable intermediate formation of the dichloro-amino-acid, thus: $R\cdot CH(NH_2)\cdot CO_2H \longrightarrow R\cdot CH(NCl_2)\cdot CO_2H \longrightarrow R\cdot CN + 2HCl + CO_2$.

On distilling a mixture of one molecular proportion of glycine and two of the sulphochloroamide, traces of hydrocyanic acid are recognisable in the distillate. When alanine is substituted for the glycine, oily drops of acetonitrile are obtained. In a similar way, *iso*valeronitrile is obtained in 70% yield from leucine and benzonitrile in 60% yield from α-aminophenylacetic acid. From histidine, cyanomethylglyoxaline is prepared, the yield being 80% of the theoretical. The substance possesses all the properties described by Pyman (T., 1911, **99**, 668). H. W. B.

Interpretations of some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valencies. VI. Further Evidence for the Electronic Formula of Benzene and the Substitution Rule. VII. Action of Sodium Methoxide on the Products of Nitration of *o*-, *p*-, and *m*-Chlorotoluenes. VIII. Further Evidence for the Electronic Tautomerism of Benzene Derivatives. HARRY SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1916, **38**, 1323—1327, 1327—1332, 1333—1338).—In earlier papers (A., 1914, i, 263, 675; 1915, i, 391) the electronic formula has been applied to the interpretation of various reactions of benzene derivatives, and a substitution rule has been advanced to the effect that substituents of the same sign or polarity will occupy meta-positions to each other, whilst those of opposite sign will occupy either ortho- or para-positions to each other.

In the present papers, Part VI. gives further evidence of the validity of the electronic formula and the substitution rule, based on the formation and behaviour of the nitro-derivatives of phenol.

In Part VII. the theory of the electronic tautomerism of benzene derivatives is supported by the results of a quantitative study of the action of sodium methoxide solutions on the nitration products of *o*-, *m*-, and *p*-chlorotoluenes. It was first proved by experiments on the action of sodium methoxide on *o*-, *m*-, and *p*-chloronitrobenzenes that, provided that the conditions admit of complete interaction, the isomerides containing negative chlorine can be estimated quantitatively by determining the amount of sodium chloride produced, and that under the same conditions the isomeride containing positive chlorine does not react. The reaction was then extended to the estimation of the percentage yields of the isomeric chloronitrotoluenes containing negative chlorine. The nitration product of *o*-chlorotoluene showed a 58·73% yield of isomerides containing negative chlorine, the nitration product of *p*-chlorotoluene a yield of 36·18%, and that of *m*-chlorotoluene a yield of 88·49%. These results are somewhat lower than those which have been obtained by physical determinations, but are sufficiently near the theoretical to substantiate the electronic tautomerism of the chlorotoluenes.

In Part VIII. the principle of electronic tautomerism is further confirmed by a consideration of the nitration of mixed dihalogenbenzenes. E. G.

Chemical Processes Involved in the Technical Reduction of Aromatic Nitro-compounds to Amino-compounds. P. N. Raikow (*Zeitsch. angew. Chem.*, 1916, **29**, i, 239—240).—In the activation of metals towards water by neutral salts due to the acid liberated by their hydrolysis, a more fundamental explanation than that previously put forward (this vol., i, 469) is afforded to account for the reduction of nitro-compounds to amines by means of iron and less than the theoretical quantity of hydrochloric acid. By the hydrolytic decomposition of the ferrous chloride initially formed by the action of the iron and hydrochloric acid, a further quantity of iron is brought into reaction and an equivalent quantity of ferrous chloride regenerated, the nascent hydrogen thereby set free reducing a further portion of the nitro-compound. The cycle of changes is represented by the following equations:

$$3Fe + 6HCl + C_6H_5{\cdot}NO_2 = 3FeCl_2 + 2H_2O + C_6H_5{\cdot}NH_2.$$

$$3FeCl_2 + 3H_2O \longrightarrow [3Fe(OH)_2 + 6HCl] + 3Fe + C_6H_5{\cdot}NO_2 = 3Fe(OH)_2 + 3FeCl_2 + 2H_2O + C_6H_5{\cdot}NH_2.$$

Confirmation of the above theory is afforded by the fact that other salts, partly hydrolysed by water, such as magnesium chloride, are likewise capable of activating the iron, and after the addition of even potassium chloride to a mixture of iron, water, and nitrobenzene which previously gave no reaction for aniline, an intense violet hypochlorite reaction is obtained. The possibility of the decomposition of ferrous chloride by the aniline, which is the essential feature of Muspratt's original explanation, becomes, therefore, in the light of the present theory, only incidental, and the basis of Wohl's objection to that explanation as a whole is accordingly removed. G. F. M.

Additive Compounds of Phenols with Organic Acids. James Kendall (*J. Amer. Chem. Soc.*, 1916, **38**, 1309—1323).—In earlier papers (A., 1914, i, 858, 1069; 1915, i, 80) an account has been given of the formation of additive compounds of strong organic acids with weak organic acids. The work has now been extended to a study of the union of phenols with organic acids, and it has been found that additive compounds are only obtained when the acidic strengths of the two components differ widely. Thus weak phenols yield oxonium salts with strong acids or with strongly acidic phenols, such as picric acid. The reaction probably represents the first stage in the formation of phenyl esters of organic acids. The additive compounds were isolated and identified by the f. p. method used in the earlier work.

With trichloroacetic acid, phenol yielded the *compound*, $C_6H_5{\cdot}OH,CCl_3{\cdot}CO_2H$, m. p. 37·6°; and *o*-, *m*-, and *p*-cresols the *compounds*, $C_6H_4Me{\cdot}OH,CCl_3{\cdot}CO_2H$, m. p. 27·0°, 14·5°, and 37·6° respectively. In the case of thymol, combination took place, but the compound could not be isolated, whilst *o*-, *m*-, and *p*-nitro-

phenols, and α- and β-naphthols showed no evidence of the formation of additive compounds.

Picric acid furnished the following compounds: with *o*-cresol, the *compound*, $C_6H_4Me\cdot OH,C_6H_2(NO_2)_3\cdot OH$, m. p. 89·8°; with *m*-cresol, the *compound*, $2C_6H_4Me\cdot OH,C_6H_2(NO_2)_3\cdot OH$, m. p. 61·6°; with *p*-cresol, the *compound*, $C_6H_4Me\cdot OH,C_6H_2(NO_2)_3\cdot OH$, m. p. 65·6°; and with thymol, the *compound*, $C_6H_3MePr^{\beta}\cdot OH,C_6H_2(NO_2)_3\cdot OH$, m. p. 96·8°. α-Naphthol also gives an additive *compound*, probably $C_{10}H_7\cdot OH,C_6H_2(NO_2)_3\cdot OH$.

Attempts to prepare compounds of weak acids with strong phenols were not successful. The experiments included picric acid with acetic acid, and *o*-, *m*-, and α-toluic acids; phenol and chloroacetic acid; and *o*-cresol and chloroacetic acid. The f. p. curves indicated that compounds were not formed in any of these cases. E. G.

6-Nitro-4-sulpho-*m*-toluic Acid and some of its Derivatives. WILLIAM J. KARSLAKE and PERRY A. BOND (*J. Amer. Chem. Soc.*, 1916, **38**, 1338—1349).—In an earlier paper (A., 1909, i, 231) the authors have shown that when 6-nitro-*m*-xylene-4-sulphonic acid is oxidised with cold alkaline potassium permanganate, the potassium salts of 6-nitro-4-sulpho-*m*-toluic, 4-nitro-6-sulpho-*m*-toluic, and 6-nitro-4-sulpho*iso*phthalic acids are produced. Karslake and Huston (A., 1909, i, 795) have studied 4-nitro-6-sulpho-*m*-toluic acid and its derivatives, and in the present paper an account is given of 6-nitro-4-sulpho-*m*-toluic acid and its derivatives.

6-*Nitro*-4-*sulpho*-m-*toluic acid*, $NO_2\cdot C_6H_2Me(SO_3H)\cdot CO_2H,3H_2O$, m. p. 94°, crystallises in plate-like needles; its *lead* and *potassium hydrogen* salts are described. The symmetrical and unsymmetrical acid chlorides have m. p. 134° and 83° respectively, instead of 133° and 93°, as stated previously (*loc. cit.*); the unsymmetrical compound has b. p. 218—220°/21 mm., or 212°/10 mm.

When the symmetrical acid chloride is treated with ammonia it is converted into the *imide*, $NO_2\cdot C_6H_2Me<\begin{matrix}CO\\SO_2\end{matrix}>NH$, m. p. 213·5°, which forms minute, plate-like needles and has a bitter taste; its *ammonium* salt, m. p. 310—320° (decomp.), and its *silver* and *potassium* salts are described. On treating the unsymmetrical chloride with ammonia, the *ammonium* salt of 6-*nitro*-4-*sulpho*-m-*toluonitrile*, m. p. 310—311° (decomp.), is produced; the *silver* and *potassium* salts were also prepared.

By the action of aniline on the symmetrical acid chloride, the anil and symmetrical dianilide were obtained. The *anil*,

$$NO_2\cdot C_6H_2Me<\begin{matrix}CO\\SO_2\end{matrix}>NPh,$$

m. p. 202—203°, crystallises in needles. The symmetrical *dianilide*, $NHPh\cdot CO\cdot C_6H_2Me(NO_2)\cdot SO_2\cdot NHPh$, m. p. 195°, forms a mass of slender needles. The action of aniline on the unsymmetrical chloride results in the formation of the symmetrical dianilide and the unsymmetrical *dianilide*, $NO_2\cdot C_6H_2Me<\begin{matrix}C(NHPh)_2\\SO_2\end{matrix}>O$, m. p. about 342° (decomp.), which crystallises in slender needles; a small

quantity of a third substance is also produced, which is probably the anilido-acid. Each of the dianilides is converted by phosphoryl chloride into the *dianil*, $NO_2\cdot C_6H_2Me<\genfrac{}{}{0pt}{}{C(NPh)}{SO_2}>NPh$, m. p. 188°, which forms bright yellow, hexagonal needles. When heated with concentrated hydrochloric acid, the dianil is transformed into the anil, and when heated with glacial acetic acid it is changed into the unsymmetrical dianilide.

*Methyl 6-nitro-*m*-toluate-4-sulphonyl chloride*,

$$NO_2\cdot C_6H_2Me(SO_2Cl)\cdot CO_2Me,$$

m. p. 101°, obtained by dissolving the unsymmetrical acid chloride in hot methyl alcohol, forms long, plate-like crystals. The corresponding *ethyl* ester has m. p. 72°.

*Methyl 6-nitro-4-sulpho-*m*-toluate*, $NO_2\cdot C_6H_2Me(SO_3H)\cdot CO_2Me$, can be obtained by boiling either of the acid chlorides with methyl alcohol and evaporating the solution; its *silver* and *barium* salts were prepared. The corresponding *ethyl* ester was also prepared.

*Dimethyl 6-nitro-4-sulpho-*m*-toluate*,

$$NO_2\cdot C_6H_2Me(SO_3Me)\cdot CO_2Me,$$

m. p. 94·5°, was obtained by heating the silver salt of methyl 6-nitro-4-sulpho-*m*-toluate with methyl iodide at 100° under pressure.

By the action of phenol on either of the acid chlorides, the *diphenyl* ester, $NO_2\cdot C_6H_2Me(SO_3Ph)\cdot CO_2Ph$, m. p. 123°, is produced, which crystallises in flat needles. E. G.

Synthesis of *p*-Cymene-2-carboxylic Acid, and of *p*-Cymene-3-carboxylic Acid, together with Certain of their Derivatives. MARSTON TAYLOR BOGERT and JOHN ROSS TUTTLE (*J. Amer. Chem. Soc.*, 1916, **38**, 1349—1368).—This work was undertaken in view of the meagre and somewhat conflicting observations hitherto made with regard to *p*-cymene-2-carboxylic acid and its derivatives, and was extended to *p*-cymene-3-carboxylic acid, as this compound had not been described.

2-Bromocymene can be best prepared in quantity by treating cymene with bromine in presence of a small amount of iron powder, but the product contains some 3-bromocymene, which cannot be removed by fractional distillation as the b. p.'s are almost identical. Pure 2-bromocymene can be obtained, but in rather poor yield, by the action of phosphorus pentabromide on carvacrol.

Cymene-2-carboxylic acid was prepared by treating an ethereal solution of 2-bromocymene with magnesium and a few drops of ethyl iodide; after keeping the resulting solution for several hours in a flask containing carbon dioxide under pressure and cooled by means of a freezing mixture, the product was decomposed with ice and hydrochloric acid and extracted with ether in the usual way. The acid has m. p. 71·7° (corr.), b. p. 171—172°/20 mm., and forms large, colourless prisms; it volatilises slowly in a current of steam, but does not sublime. The sodium, potassium, calcium, barium, copper, and silver salts are described. The *methyl* ester, b. p. 132°/16·2 mm., is a colourless oil with a pleasant odour; the *ethyl* ester

was also prepared. The *acid chloride*, b. p. 131·5—132°/17·7 mm., or 135·5—136°/21·5 mm., is a clear, colourless, pungent-smelling liquid. The *amide*, m. p. 147° (corr.), crystallises in microscopic needles, and the *anilide*, m. p. 143·5° (corr.), in small, colourless prisms. 2 : 2′-*Dimethyl*-5 : 5′-*di*-iso*propyldibenzoylhydrazine*,

$$[CHMe_2\cdot C_6H_3Me\cdot CO\cdot NH\cdot]_2,$$

m. p. 192° (corr.), obtained by the action of hydrazine hydrate on a solution of the acid chloride in ether, forms minute, colourless prisms; when heated for one and three-quarter hours at 260—280° it is converted into 2 : 5-*di*-2′-p-*cymyl*-1 : 3 : 4-*oxadiazole*,

$$CHMe_2\cdot C_6H_3Me\cdot C\ll\genfrac{}{}{0pt}{}{N\cdot N}{--O--}\gg C\cdot C_6H_3Me\cdot CHMe_2,$$

m. p. 111·5° (corr.), which crystallises in small, colourless prisms. When the acid chloride is added slowly to an ethereal solution of ethyl aminoacetate, *ethyl* 2-*methyl*-5-iso*propylhippurate* is obtained as an oil, which on hydrolysis furnishes 2-*methyl*-5-iso*propylhippuric acid*, $CHMe_2\cdot C_6H_3Me\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 183° (corr.), which forms colourless, glassy scales.

On repeating the work of Paterno and Fileti (this Journal, 1876, i, 595) and Paterno and Spica (A., 1880, 163) it was found that the acid obtained by the latter authors by fusing the amide with potassium hydroxide or by heating it with concentrated hydrochloric acid at 180° was impure cymene-2-carboxylic acid.

p-*Cymene*-3-*carboxylic acid*, m. p. 84° (corr.), b. p. 285° (corr.), prepared from 3-bromocymene by the method used in the case of *p*-cymene-2-carboxylic acid, forms colourless needles and is readily volatile with steam; its *sodium*, *potassium*, *barium*, *calcium*, *copper*, and *silver* salts are described. The *methyl* ester, b. p. 128—129°/13·5 mm., is a colourless liquid with a pleasant odour; the *ethyl* ester has b. p. 141—142°/13·5 mm., and the *phenyl* ester, b. p. 199—208°/22·5—24·5 mm. The *acid chloride*, b. p. 115—116°/9·2 mm., or 128—129°/20·1 mm., is a colourless, mobile liquid of penetrating odour. The *amide*, m. p. 137·5° (corr.), and the *anilide*, m. p. 151° (corr.), form colourless, silky needles. 3 : 3′-*Dimethyl*-6 : 6′-*di*iso*propyldibenzoylhydrazine*, m. p. 213·5° (corr.), crystallises in colourless, silky needles, and when heated for two hours at 200° is converted into 2 : 5-*di*-3′-p-*cymyl*-1 : 3 : 4-*oxadiazole*, m. p. 132·5° (corr.), which forms long, colourless needles. When the diacylhydrazine is treated with phosphorus pentachloride, a mixture of the hydrazide chloride and furodiazole is produced, which, on being heated at 170° for half an hour, yields 2 : 5-*di*-3′-p-*cymyl*-1-*phenyl*-1 : 3 : 4-*triazole*,

$$CHMe_2\cdot C_6H_3Me\cdot C\ll\genfrac{}{}{0pt}{}{N\cdot N}{NPh}\gg C\cdot C_6H_3Me\cdot CHMe_2,$$

m. p. 182·5° (corr.), which forms small, colourless crystals. 3-*Methyl*-6-iso*propylhippuric acid*, m. p. 205·5° (corr.), crystallises in colourless, pearly scales. E. G.

Derivatives, especially Esters and Acetyl Compounds, of Opianic, Bromo- and Nitro-opianic Acids. RUD. WEGSCHEIDER and ERNST SPÄTH (*Monatsh.*, 1916, **37**, 277—303).—Typical reac-

tions of *o*-aldehydic acids, and especially the isomerisation of the esters, are exhibited by opianic acid and its bromo- and nitro-derivatives.

It was found earlier that nitro-opianic acid yields a diacetyl compound (1908), and therefore opianic acid was left with a mixture of acetic anhydride and concentrated sulphuric acid in order to see whether it would behave likewise. Although the conditions were most favourable to the condensation of acetyl residues with the aldehyde group, only the mono-acetyl derivative of the hydroxylactone form, m. p. 112—113°, could be isolated. This is very easily transformed into opianic anhydride under the influence of traces of mineral acids, which suggests that the anhydride is not a true acid anhydride, but has the constitution,

$$\left[C_6H_2(OMe)_2{<}{\begin{smallmatrix}CH-\\CO-\end{smallmatrix}}{>}O\right]_2O.$$

Methyl ψ-opianate is converted into acetylopianic acid when left with acetic anhydride and a drop of concentrated sulphuric acid, but the true methyl opianate yields the *di-acetate*,

$$CO_2Me\cdot C_6H_2(OMe)_2\cdot CH(OAc)_2,$$

which crystallises in large leaflets, m. p. 88—89°. This is not affected by boiling methyl alcohol, but is hydrolysed by boiling water or very dilute potassium hydroxide to methyl opianate, whilst hydrolysis with sodium methoxide solution or methyl-alcoholic hydrogen chloride solution gives rise to a mixture of the normal and ψ-esters with a little opianic acid. In the preparation of the di-acetate, prolonged action of acetic anhydride must be avoided, for this leads to the formation of acetylopianic acid. The great tendency to the closing of the lactone ring is exhibited in these reactions.

In the case of bromo-opianic acid, it is found that the normal methyl ester is more easily hydrolysed by boiling water than is methyl opianate, but that the tendency to the formation of the ψ-ester is much less. Methyl ψ-bromo-opianate can be readily obtained by brominating the ψ-opianate, but true methyl opianate is very resistant to the influence of bromine. If the bromination is forced, the hydrogen bromide which is liberated causes rearrangement into the ψ-esters or even hydrolysis to bromo-opianic acid.

Methyl *n*-bromo-opianate yields a *diacetate*,

$$CO_2Me\cdot C_6HBr(OMe)_2\cdot CH(OAc)_2,$$

when left with acetic anhydride and a drop of sulphuric acid. This forms long, six-sided, rhombic prisms [$a:b=1:0{\cdot}591$], m. p 132—132·5°, and is not so readily hydrolysed as the diacetate of methyl opianate, whilst methyl bromo-opianate is less resistant than methyl opianate. When the acetate is boiled for some time with water or dilute alkali, it is therefore slowly converted into the free bromo-opianic acid as well as the methyl ester. Methyl-alcoholic hydrogen chloride hydrolyses the acetate to the ψ-ester. If methyl bromo-opianate is left longer with acetic anhydride and sulphuric acid, it yields *acetylbromo-opianic acid*, $C_6HBr(OMe)_2{<}{\begin{smallmatrix}CH\cdot OAc\\CO\end{smallmatrix}}{>}O$, in long needles, m. p. 116°, which is readily converted into bromo-

opianic anhydride, m. p. 256—258°, when heated alone at 200° or with metaphosphoric acid at 180—190°. Bromo-opianic acid is also readily dehydrated by the latter method.

Methyl ψ-bromo-opianate forms acetylbromo-opianic acid when left with acetic anhydride and sulphuric acid.

Normal *ethyl bromo-opianate*, $CHO\cdot C_6HBr(OMe)_2\cdot CO_2Et$, is obtained from the silver salt in long needles, m. p. 74—75°, and forms a *diacetate*, large, glistening crystals, m. p. 131—132°.

In the preparation of the true esters from the silver salts it is best to avoid ionising solvents. Thus, good yields of methyl nitro-opianate, m. p. 78°, and *ethyl nitro-opianate*, yellow, monoclinic needles and tablets [$a:b:c = 0{\cdot}4710:1:0{\cdot}5351$, $\beta = 111°51'$], m. p. 80—81°, may be obtained if cold chloroform is used as the diluent. These esters readily form the known diacetates, but if the action of acetic anhydride and sulphuric acid is prolonged more than ten minutes or so they are transformed into acetylnitro-opianic acid.

J. C. W.

Benzaldehyde-*o*-sulphonic Acid. ISIDOR GOLDBERGER (*Monatsh.*, 1916, **37**, 125—135).—Directions for the preparation of pure sodium benzaldehyde-*o*-sulphonate from the technical material are given. The salt crystallises from alcohol in long prisms with $1H_2O$.

The chief product of the action of phosphorus pentachloride on this salt is the chloride, $C_6H_4{<}{\begin{smallmatrix}CHCl\\-SO_2-\end{smallmatrix}}{>}O$ (List and Stein, *Ber.*, 1898, **31**, 1668); this is frequently accompanied by a substance richer in chlorine, which can be decomposed by boiling with methyl alcohol. High yields of the monochloride are obtained by grinding the dried salt with 1·5 times its weight of phosphorus pentachloride. It has m. p. 114—115·5°, and forms well-developed monoclinic crystals [$a:b:c = 0{\cdot}5774:1:0{\cdot}6515$, $\beta = 90°29'$]. It is very stable towards methyl alcohol, and only reacts to any extent with phosphorus pentachloride at about 180°, when it behaves as a true sulphonyl chloride, forming *o*-chlorobenzylidene chloride and *o*-chlorobenzoic acid.

The free benzaldehyde-*o*-sulphonic acid was obtained by boiling the above chloride with water. The *silver* salt was prepared from this and boiled with methyl iodide, but no pure methyl ester could be isolated. It seemed possible that the aldehyde group might have reacted with the alcohol, but the free acid was found to be quite indifferent to the action of methyl alcohol.

The sodium salt was also treated with methyl sulphate, whereby many products were formed, the only recognisable one being the sulphone of 1-methoxybenzene-2-sulphonic acid, m. p. 113° (*ibid.*), which is produced by boiling the salt with an excess of the reagent.

J. C. W.

Photochemical Reactions of Phenylnitroindones. V. Transformation Products of Phenyl-*o*-nitroindone. M. BAKUNIN and F. GIORDANI (*Gazzetta*, 1916, **46**, ii, 42—51).—Cryoscopic measurements in naphthalene of the polymeride obtained by exposure of

phenyl-*o*-nitroindone to sunlight, and subsequently separated by distillation in a current of carbon dioxide, show that it is at least trimeric, and that it probably contains the tetrameride.

T. H. P.

Volatile Oil of Euthamia Caroliniana (L.), Greene. G. A. RUSSELL (*J. Amer. Chem. Soc.*, 1916, **38**, 1398—1402).—The fresh herb *Euthamia Caroliniana* on distillation yielded 0·693% of a pale yellow, volatile oil with a pleasant aromatic odour. The oil had D^{23} 0·8587, n_D 1·4805, $[\alpha]_D^{23}$ $-10°48'$, saponification number 6·35 (equivalent to 2·10% of esters, calculated as $C_{10}H_{17}\cdot OAc$), acetylation number, 25·3 (indicating the presence of 5·35% of free alcohols, calculated as $C_{10}H_{17}\cdot OH$), and was soluble in six volumes of 90% alcohol or nine volumes of 70% alcohol.

The oil consisted chiefly of dipentene, with a trace of pinene and possibly a little limonene. There were no free acids present, and the combined acids were probably formic and acetic. The oil also contained aldehydes and about 10% of a compound or compounds of lævorotatory character and comparatively high density.

E. G.

Chemical Composition of Pyocyanin. A. MADINAVEITIA (*Anal. Fis. Quim.*, 1916, **14**, 263—266).—The results of analysis indicate that pyocyanin, present in the *Bacillus pyocyaneus*, has the empirical formula $C_{60}H_{59}O_3N_{10}Cl_5$, although such physical characteristics as solubility and crystallisation point to a smaller molecular weight.

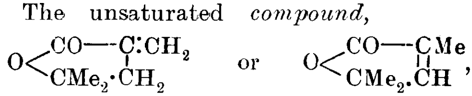
A. J. W.

Reactions of Lactones. II. MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1916, **37**, 37—51. Compare A., 1914, i, 74).—When 4-hydroxy-5-keto-2 : 2 : 4-trimethyltetrahydrofuran is treated with magnesium phenyl bromide in dilute solution and the product carefully decomposed by dilute acetic acid, it yields *αα-diphenyl-βδ-dimethylpentane-αβδ-triol*,

$$OH\cdot CMe_2\cdot CH_2\cdot CMe(OH)\cdot CPh_2\cdot OH,$$

b. p. 232—238°/12 mm., which is readily dehydrated by boiling with 45% sulphuric acid. Further reactions of the anhydride (4-hydroxy-5 : 5-diphenyl-2 : 2 : 4-trimethyltetrahydrofuran) are now recorded. It does not react with hydroxylamine or magnesium phenyl bromide, but it readily parts with water when distilled under reduced pressure with a few drops of 45% sulphuric acid, yielding a *compound*, $C_{19}H_{20}O$, b. p. 194—195°/18 mm., with a faint aromatic odour.

4-Hydroxy-5-keto-2 : 2 : 4-trimethyltetrahydrofuran yields an *acetate*, $C_9H_{14}O_4$, b. p. 135—136°/15 mm., but fuming hydrobromic acid causes the elimination of water, rather than the formation of a bromide. The unsaturated *compound*,



which results crystallises in glistening tablets and prisms, m. p.

53—56°, b. p. 86°/10 mm., and reacts with magnesium methyl iodide to form a diol, the *anhydride* of which,

$$O<\begin{matrix}CMe_2\cdot C{:}CH_2\\ \vert \\ CMe_2\cdot CH_2\end{matrix} \quad \text{or} \quad O<\begin{matrix}CMe_2\cdot CMe\\ \Vert \\ CMe_2\cdot CH\end{matrix},$$

has b. p. 125—128°, and smells like camphor.

γ-Amino-$\beta\gamma\epsilon$-trimethylhexane-$\beta\epsilon$-diol forms a *picrate*, m. p. 134—137°, and is transformed by boiling with 45% sulphuric acid into the anhydride, 3-*amino*-2 : 2 : 3 : 5 : 5-*pentamethyltetrahydrofuran*, $O<\begin{matrix}CMe_2\cdot CMe\cdot NH_2\\ \vert \\ CMe_2\cdot CH_2\end{matrix}$, which yields the following derivatives: *picrate*, m. p. 192—194°; *phenylthiocarbamide*, $C_{16}H_{24}ON_2S$, tufted needles, m. p. 134—136°; *benzyl-*, $C_9H_{17}O\cdot NH\cdot CH_2Ph$, b. p. 157—161°/10 mm. (*picrate*, m. p. 190—192°; *nitroso*-compound, short columns, m. p. 58—61°).

4-Amino-5 : 5-diphenyl-2 : 2 : 4-trimethyltetrahydrofuran also forms a *picrate*, long, thin, prismatic needles, m. p. 183—186°, and a *phenylthiocarbamide*, $C_{26}H_{28}ON_2S$, granules, m. p. 162—164°.

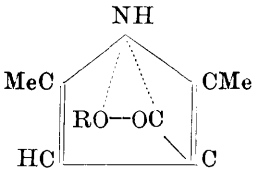
J. C. W.

The Mechanism of the Saponification of Pyrrole Derivatives. G. Korschun (*Bull. Soc. chim.*, 1916, [iv], **19**, 164—191).—The first part of the paper is a summary of the work already published on this subject.

[With A. Gounder.]—A quantitative study of the saponification of a number of substituted pyrrole-mono- and -di-carboxylic ethyl esters. In the case of ethyl 2 : 5-dimethylpyrrole-3-carboxylate the replacement of the hydrogen atom attached to the nitrogen atom by an amino-group produces a marked increase in the velocity of saponification, a slightly greater increase is obtained by substituting a methyl group, and a very much greater increase with a phenyl group. The same holds good to a lesser degree for 2 : 5-dimethylpyrrole-3 : 4-dicarboxylic esters. The replacement of a hydrogen atom in position 4 in 1 : 2 : 5-trimethylpyrrole-3-carboxylic ester by a methyl group produces a diminution in the velocity of saponification, the diminution being slightly less if it is substituted in 1-amino-2 : 5-dimethylpyrrole-3-carboxylic ester. Other conditions being the same, a carbethoxy-group is much more readily saponified when in the position α than in the position β, and is much less readily saponified when it is between two side-chains. Under identical conditions the carbethoxy-groups in the α-position in pyrrole-mono- and -di-carboxylic esters are saponified with practically equal velocities. The second carbethoxy-group in the 3 : 4-dicarboxylic esters is much more difficult to saponify than the first. The substitution of two phenyl groups for the two methyl groups in ethyl 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate causes a marked diminution in the velocity of saponification. The replacement of the hydrogen atom attached to nitrogen in this ester by the carbamido-group produces a diminution in the velocity of saponification.

The replacement of the hydrogen atom attached to nitrogen in ethyl 2 : 5-dimethylpyrrole-3 : 4-dicarboxylate by a methyl group

facilitates the saponification of the first carbethoxy-group, but renders more difficult that of the second group. The substitution of an amino-group for the methyl group makes the saponification of the second carbethoxy-group still more difficult.



Certain of these facts can be explained on the basis of the intramolecular formation of a nucleus by means of the partial valencies (annexed formula) (compare Palomaa, A., 1914, i, 136), but it is equally possible that it may be necessary to adopt the constitutional formula proposed by Ciamician for pyrrole and its derivatives (compare A., 1906, i, 104). It is proposed to examine this question more closely by a spectrographic study of the compounds. W. G.

Derivatives of Isatin and Dioxindole. VI. MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1916, **37**, 25—35. Compare A., 1914, i, 81).—The expectation that the product of the action of acetic anhydride and zinc dust on isatin is tetra-acetylisatide (A., 1912, i, 800) has been confirmed by acetylating isatide.

Directions are given for the preparation of pure 1-methylisatin from isatin.

The product of the action of phosphorus pentachloride on 1-methylisatin (*ibid.*) is now recognised as Colman's 3 : 3-dichloro-1-methyloxindole (T., 1889, **55**, 4). It gradually dissolves in warm 10% potassium hydroxide to form potassium 1-methylisatate, and is converted into 1-methylisatin by boiling with water. 5-Bromo-1-methylisatin (A., 1913, i, 757) is similarly converted into 3 : 3-*dichloro*-5-*bromo*-1-*methyloxindole*, $C_6H_3Br{<}{CCl_2 \atop NMe}{>}CO$, a grey powder, m. p. 126°, by the agency of phosphorus pentachloride.

Silver 1-methylisatate was warmed with methyl iodide in the hope of obtaining methyl 1-methylisatate, but, although reaction readily took place, the only product which could be isolated was 1-methylisatin. Obviously, the expected ester had suffered the loss of methyl alcohol.

7-Methylisatin (Bauer, A., 1907, i, 603) was converted by the action of magnesium phenyl bromide into 3-*phenyl*-7-*methyldioxindole*, $C_6H_3Me{<}{CPh(OH) \atop NH}{>}CO$, short needles, m. p. 174°, which yielded the methyl ether of 3-*phenyl*-1 : 7-*dimethyldioxindole*, glistening needles, m. p. 97°, on treatment with methyl sulphate.
J. C. W.

3-Nitro- and 3-Aminocarbazolemonosulphonic Acids and their Derivatives Alkylated at the Pyrrole Nitrogen Atom. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 291023; from *J. Soc. Chem. Ind.*, 1916, **35**, 685).—3-Nitrocarbazole is converted almost entirely into the monosulphonic acid when it is sulphonated in suspension or solution in nitrobenzene at 0—5° with a solution of chlorosulphuric acid in the same solvent. The temperature is allowed to rise slowly to 20°, and after keeping some time

the mixture is poured into water, the nitrobenzene layer separated, and the nitrocarbazolesulphonic acid recovered from the aqueous solution as its sodium salt. The corresponding amino-compound is obtained by reduction. G. F. M.

Formation of 1-Phenyl-4-benzyl-3-methylpyrazolone. MICHELE GIUA (*Gazzetta*, 1916, **46**, ii, 61—65).—In alcoholic solution containing a little acetic acid, methyl or ethyl benzylacetoacetate reacts in the hot with phenylhydrazine more readily than would be expected from the results of Michaelis, Voss, and Greiss (A., 1901, i, 407), 1-phenyl-4-benzyl-3-methylpyrazolone being formed. Under similar conditions, methyl dibenzylacetoacetate does not react with phenylhydrazine, owing to the steric hindrance caused by the two benzyl groups united to the carbonyl group. A similar case was observed by Petrenko-Kritschenko, who found that acetonedicarboxylic derivatives of the type $CO_2Et\cdot CR_2\cdot CO\cdot CR_2\cdot CO_2Et$ or $CO_2Et\cdot CHR\cdot CO\cdot CHR\cdot CO_2Et$ react with neither phenylhydrazine nor phosphorus pentachloride, whereas the ester,

$$CO_2Et\cdot CH_2\cdot CO\cdot CHMe\cdot CO_2Et,$$

reacts with phenylhydrazine, giving the phenylhydrazone, from which the phenyldimethylpyrazolone can be obtained (A., 1896, i, 258).

Methyl benzylacetoacetate forms an oil, b. p. 180—182°/15 mm., D^{17} 1·091, and in alcoholic solution gives a violet coloration with ferric chloride.

Methyl dibenzylacetoacetate forms an oil, b. p. 235—238°/18 mm., and in alcoholic solution gives a dark red coloration with ferric chloride. T. H. P.

Pyrimidines. LXXVIII. Reduction of 6-Chloro-2-thiolpyrimidines. TREAT B. JOHNSON and A. WILLARD JOYCE (*J. Amer. Chem. Soc.*, 1916, **38**, 1385—1392).—In an earlier paper (A., 1915, i, 1003) the authors have shown that 6-chloro-2-thiolpyrimidines are readily reduced by zinc dust with formation of the corresponding 2-thiolpyrimidines, and have described the preparation in this way of 2-ethylthiolpyrimidine, 2-ethylthiol-4-methylpyrimidine, and 5-ethoxy-2-ethylthiolpyrimidine. In continuing this work it has been found that such compounds can be easily prepared in quantity by this method.

2-Methylthiolpyrimidine, $N{<}\begin{matrix}C(SMe)\cdot N\\ CH{=\!=}CH\end{matrix}{>}CH$, b. p. 99—100°/14 mm., obtained by heating 6-chloro-2-methylthiolpyrimidine with zinc dust and dilute alcohol, is a colourless oil with an odour resembling that of pyridine; the *hydrochloride*, m. p. 147°, and *hydrobromide*, m. p. 187°, are described. The pyrimidine combines with methyl iodide to form the *methiodide*,

$$N{<}\begin{matrix}C(SMe)\cdot N(MeI)\\ CH{=\!=\!=\!=}CH\end{matrix}{>}CH,$$

m. p. 146—147°, which crystallises in prismatic needles. The *methiodide* of 2-ethylthiolpyrimidine has m. p. 135°.

When 2-ethylthiolpyrimidine is reduced with sodium and alcohol it yields trimethylenediamine and methyl mercaptan.

Wheeler and Liddle (A., 1909, i, 61) have shown that when 2-thiouracil is treated with benzyl chloride in presence of potassium hydroxide, 2-benzylthioldihydropyrimid-6-one is produced. It has now been found that a small quantity of *2-benzylthiol-3-benzyldihydropyrimid-6-one*, m. p. 144—145°, is also produced in this reaction, and forms flat, colourless prisms. When 2-benzylthioldihydropyrimid-6-one is heated with concentrated hydrochloric acid it is converted into *2-thio-3-benzyltetrahydropyrimid-6-one*,

$$CH_2Ph\cdot N<\begin{matrix}CS-NH\\CH:CH\end{matrix}>CO,$$

m. p. 231°, which crystallises in plates, and when digested with chloroacetic acid is converted into 3-benzyltetrahydropyrimid-2:6-dione. By the action of phosphoryl chloride on 2-benzylthioldihydropyrimid-6-one, *6-chloro-2-benzylthiolpyrimidine*, m. p. 48—49°, b. p. 210°/18 mm., is produced, which forms long prisms and is hydrolysed by concentrated hydrochloric acid with formation of uracil. Attempts were made to reduce this chloropyrimidine, but without success; it combines with hydriodic acid to form the *hydriodide*, m. p. 136°. E. G.

The Diketotriazines. Synthesis of 4-Alkyl Derivatives of Semicarbazide. J. Bougault (*Ann. Chim.*, 1916, [ix], **5**, 317—345). —A résumé of work already published (compare A., 1914, i, 1004, 1205; 1915, i, 598). W. G.

4:4′-Azoxyphthalic Acid. Georg Sachs (*Monatsh.*, 1916, **37**, 53—56).—When ethyl 4-nitrophthalate is energetically treated with alcoholic potassium hydroxide it is converted into *4:4′-azoxyphthalic acid*, $C_{16}H_{10}O_9N_2$, which crystallises from water as a salmon-coloured powder, which seems to melt at about 228° and again with vigorous decomposition at 280—310°. The *tetramethyl* ester is orange-red and has m. p. 103—104°. The same acid results if free 4-nitrophthalic acid is heated for some hours with concentrated alcoholic potassium hydroxide on a briskly-boiling water-bath. J. C. W.

4:4′-Azo- and 4:4′-Azoxy-phthalic Acids. Isidor Goldberger (*Monatsh.*, 1916, **37**, 57—58).—In attempting to reduce 4-nitrophthalic acid to 4:4′-azoxyphthalic acid by Sach's method (preceding abstract) the author sometimes obtained 4:4′-azophthalic acid (Bogert and Boroschek, A., 1902, i, 98). *Tetramethyl 4:4′-azophthalate* is yellowish-red, has m. p. 124—126°, and does not depress the m. p. of the azoxyphthalate. J. C. W.

Azohydroxamic Acids. II. G. Ponzio (*Gazzetta*, 1916, **46** ii, 56—60. Compare A., 1915, i, 1011).—The reaction by which phenylazoformhydroxamic acid is obtained from the benzenediazonium derivative of trinitromethane has now been extended to other diazonium salts of trinitrotoluene, the results obtained confirming the earlier statements concerning the method of formation and the properties of azohydroxamic acids. The salts were obtained

by treatment of the potassium salt of trinitromethane, in dilute aqueous solution, with the aryldiazonium acetate and are all yellow and almost insoluble in water or ether; in contact with the latter and a little water, they gradually dissolve with liberation of nitrous fumes and formation of the arylazoformhydroxamic acids.

p-*Tolylazoformhydroxamic acid*, $C_6H_4Me\cdot N\colon N\cdot CO\cdot NH\cdot OH$, forms shining, straw-yellow prisms, m. p. 102°, dissolves unchanged in concentrated sulphuric or nitric acid, and when heated with dilute sodium hydroxide solution, yields *p*-tolylazoimide, which is volatile in a current of steam.

o-*Chlorophenylazoformhydroxamic acid*, $C_6H_4Cl\cdot N\colon N\cdot CO\cdot NH\cdot OH$, forms shining, white, flattened needles, m. p. 71°, and yields *o*-chlorophenylazoimide, which is volatile in a current of steam, when heated with dilute sodium hydroxide solution.

2 : 4-*Dichlorophenylazoformhydroxamic acid*,

$$C_6H_3Cl_2\cdot N\colon N\cdot CO\cdot NH\cdot OH,$$

forms slender, white needles with straw-yellow reflection, m. p. 95°.

2 : 4-*Dichlorophenylazoimide*, $C_6H_3N_3Cl_2$, obtained either from the preceding compound or, in poor yield, by the interaction of 2 : 4-dichlorobenzenediazonium chloride with hydroxylamine hydrochloride, forms straw-yellow needles, m. p. 54—55°, and is volatile in a current of steam.

2 : 4 : 6-*Tribromophenylazoformhydroxamic acid*,

$$C_6H_2Br_3\cdot N\colon N\cdot CO\cdot NH\cdot OH,$$

forms white prisms with straw-yellow reflection, m. p. 171—172°. When distilled with dilute sodium hydroxide solution or reduced by means of zinc dust and acetic acid, it yields 2 : 4 : 6-tribromoaniline, which is slightly volatile in a current of steam, its behaviour being, therefore, different from that of the other members of the series.

2 : 4 : 6-Tribromophenylazoimide, prepared according to Forster and Fierz's method (T., 1907, **91**, 1952), has m. p. 72° and distils slowly in a current of steam.

The *o*-tolyldiazonium salt of trinitromethane dissolves gradually in moist ether with liberation of nitrous fumes and formation of 3-nitro-*o*-cresol. T. H. P.

Reactions of Nitrates of Hydroxyazo-compounds. G. CHARRIER (*Gazzetta*, 1916, **46**, ii, 1—17, and *Atti R. Accad. Sci. Torino*, 1915–1916, **51**, 678—694).—The nitrates of ethers of arylazo-β-naphthols undergo decomposition into hydroxyazo-compound, alkyl nitrate, and nitric acid when they are dissolved in any alcohol and the solution left for some time. That the reaction is not to be interpreted as a hydrolysis, $OR\cdot C_{10}H_6\cdot N\colon NAr,2HNO_3 + H_2O \longrightarrow OH\cdot C_{10}H_6\cdot N\colon NAr + R\cdot OH + 2HNO_3$, or as an alcoholysis,

$$OR\cdot C_{10}H_6\cdot N\colon NAr,2HNO_3 + R'OH \longrightarrow OH\cdot C_{10}H_6\cdot N\colon NAr + R'NO_3 + ROH + HNO_3,$$

is shown by the fact that the action of absolute methyl alcohol on

the nitrate of 1-benzeneazo-2-naphthyl ethyl ether yields only 1-benzeneazo-2-naphthol, ethyl nitrate, and nitric acid,

$$OEt\cdot C_{10}H_6\cdot N{:}NPh,2HNO_3 \longrightarrow OH\cdot C_{10}H_6\cdot N{:}NPh + Et\cdot NO_3 + HNO_3.$$

Comparison of this method of decomposition with the diazo-scission of the same nitrates,

$$OR\cdot C_{10}H_6\cdot N{:}NAr,2HNO_3 \longrightarrow OR\cdot C_{10}H_6\cdot NO_2 + N{:}NAr\cdot NO_3 + H_2O,$$

supports the structure which the author attributes to these salts of azo-compounds, namely, $NO_2\cdot O\cdot OHR\cdot C_{10}H_6\cdot N{:}NHAr\cdot O\cdot NO_2$.

The nitrates of various arylazo-β-naphthyl ethers have been treated with concentrated halogen hydracids. The almost complete diazo-scission first occurring under these conditions is followed by decomposition of the diazonium nitrate, which loses nitrogen and yields the halogen derivative with the halogen atom in place of the diazo-group. Thus, the action of boiling concentrated halogen hydracids on these nitrates is represented thus:

$$OR\cdot Ar''\cdot N_2Ar',2HNO_3 \longrightarrow OR\cdot Ar''\cdot NO_2 + N{:}NAr'\cdot NO_3$$

and $N{:}NAr'\cdot NO_3 + HX \longrightarrow Ar'X + HNO_3 + N_2$. To a slight extent the diazonium nitrate formed also undergoes secondary decompositions represented by the schemes:

$$N{:}NAr'\cdot NO_3 + H_2O \longrightarrow Ar'\cdot OH + N_2 + HNO_3$$

and $2N{:}NAr'\cdot NO_3 \longrightarrow 2Ar'\cdot NO_2 + 2N_2 + O_2$. Further, with those nitrates in which the para-position of the non-hydroxylated nucleus is free, the hydroxyazo-compound undergoes nitration with formation of a *p*-nitrohydroxyazo-compound; the extent to which this nitration takes place increases with the concentration of the nitrate of the etherified hydroxyazo-compound in the halogen hydracid.

T. H. P.

Nitrated Proteins. V. Hydrolysis of Nitrofibroin with Hydrochloric Acid. TREAT B. JOHNSON and ARTHUR J. HILL (*J. Amer. Chem. Soc.*, 1916, **38**, 1392—1398).—Johnson, Hill, and O'Hara (A., 1915, i, 1017) have given an account of the preparation of nitrofibroin by the action of nitric acid (D 1·12) on silk fibroin. The present investigation was undertaken in order to ascertain whether the tyrosine in fibroin suffers further change by long exposure to the action of the nitric acid with formation of 3:5-dinitrotyrosine (Johnson and Kohmann, A., 1915, i, 1060), and to determine the nature of the other α-amino-acids of nitrofibroin.

On heating nitrofibroin with hydrochloric acid (D 1·19) at 120—130° for fifteen hours, the amino-acids formed (calculated as percentages of the nitrofibroin) were as follows: glycine, 25·36; 3-nitrotyrosine, 5·74; alanine, 10·0. Nitrofibroin has approximately the same rotatory power as fibroin, the values obtained for $[\alpha]_D^{17}$ being $-43·39°$ and $-44·10°$; its hydrolysis, however, leads to the formation of inactive alanine and 3-nitrotyrosine.

The prolonged action of nitric acid (D 1·12) on nitrofibroin

yielded only the end-products of oxidation, namely, oxalic acid and ammonium nitrate. E. G.

Brain Kephalin. II. Fatty Acids. C. G. MACARTHUR and L. V. BURTON (*J. Amer. Chem. Soc.*, 1916, **38**, 1375—1382).—In an earlier paper (A., 1914, i, 1197) an account was given of the extraction of brain kephalin and of the forms in which its nitrogen is present.

It is now shown that about 66% of kephalin is in the form of fatty acids, and that the kephalins from sheep and ox brains are very similar with respect to both the kind and amount of acids present. Of the total acids, more than 50% is oleic, more than 25% stearic, about 10% kephalinic, and 5% clupanodonic acid. The variation in the amount of these acids in different preparations indicates the existence of mixed kephalins which are closely associated. Experiments on the bromination of kephalinic acid suggest that it is probably a hydroxypalmitic acid, but the evidence for the identity of this acid and for that of clupanodonic acid is not conclusive. E. G.

Acid Hæmochromogen. CH. DHÉRÉ and G. VEGEZZI (*Compt. rend.*, 1916, **163**, 18—20).—Acid hæmochromogen can readily be obtained by shaking a very slightly acid, aqueous alcoholic solution of hæmatin in a sealed tube with a little powdered sodium hyposulphite. The solution obtained is of a deep red colour, and remains quite limpid for two months in the sealed tube. Its absorption spectrum has three bands, namely, α, extending from λ 571·5 to 557·0 $\mu\mu$; β, from λ 535·0 to 520·5 $\mu\mu$; and γ, from λ 417·0 to 399·0 $\mu\mu$. In their sharpness, intensity, and breadth these bands resemble those of alkaline hæmochromogen, but the α- and β-bands are displaced towards the red and the γ-band towards the ultra-violet. W. G.

Physiological Chemistry.

Enzymic Actions of Blood on Dextrose. I. Destruction and Condensation of Dextrose by Normal Blood. UGO LOMBROSO (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 736—741).—The reducing power of normal dog's blood, to which 0·5—1% of dextrose has been added, undergoes gradual diminution, but in the early stages of the change is restored to its original value by hydrolysis with hydrochloric acid. This phenomenon is regarded as due to condensation of the dextrose or to its combination with proteins. After eighteen to twenty-four hours (at 38°) the quantity of such condensed dextrose present diminishes. These results furnish an explanation of the diverse views which have been expressed concerning the glucolytic power of blood. T. H. P.

Variations in the Blood Sugar in Health. GEORGE GRAHAM (*J. Physiol.*, 1916, **50**, 285—295).—A dose of 100 grams of dextrose produces a sudden rise in the blood sugar in adult men, which begins in ten minutes, reaches its maximum in twenty minutes, and disappears in one to one and a-half hours. Fatigue causes a higher maximum and delayed disappearance. The "extra" sugar is not considered to be due to a failure of the liver, but is considered to be on its way to the muscles and other store-houses. G. B.

Glycolysis in Diabetic Blood with a Method for the Estimation of Blood Sugar. HUGH MACLEAN (*J. Physiol.*, 1916, **50**, 168—181).—A modification of Bang's method for the estimation of sugar in blood (compare A., 1907, ii, 136; 1908, ii, 235, 739). Instead of estimating the cuprous oxide by adding standard iodine, iodine and potassium iodide are present at the outset in the alkaline copper solution, and the iodine liberated after addition of hydrochloric acid is titrated with $N/250$-thiosulphate solution. A table is given showing the thiosulphate corresponding with hundredths of milligrams of dextrose up to 2 mg.

It is shown that the glycolytic power of diabetic blood is not inferior to that of normal blood, so that, if the mechanism of blood destruction in the tissues is the same, diabetic tissues also possess the power to destroy sugar. G. B.

The Chemistry and Physiology of the Coagulation of the Blood. II. Fibrinogen Solutions, Thrombin, and its Constituents. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1916, **76**, 145—188).—To bring fibrinogen into colloidal solution the presence of certain protein degradation products is necessary. These products effect solution, not in the free state, but as combinations with sodium chloride. If they are converted into calcium chloride compounds, they no longer bring about solution, but being absorbed by the protein particles they produce precipitation of the same (clotting). Many degradation products have a marked capacity to form calcium chloride compounds, and produce in this way the precipitation of fibrinogen. These are designated *serozymes*, or thrombin when they are already combined with calcium chloride; thrombin, according to this conception, is therefore a calcium chloride compound of certain degradation products of proteins. They are formed in plasma or serum by hydrolysis of proteins. Hence, all agents which favour hydrolysis (dilution with water or sodium chloride solution, $N/300$-hydrochloric acid, sodium glycocholate, certain protein degradation products) favour the serozyme character of a serum. If hydrolysis proceeds too far, the serozyme properties are injured. In egg-white and saliva serozyme substances can be detected. *Cytozymes* are substances which promote the thrombin action in sera containing serozymes. They act either by virtue of their chemical character or by their surface action (adsorption; thromboplastic substances). Many combine both kinds of action (lipoid emulsions). S. B. S.

Concentration of Antitoxic Sera. ANNIE HOMER (*Biochem. J.*, 1916, **10**, 280—307).—In the new method devised by Banzhaf for the concentration of antitoxic sera, the diluted serum or plasma containing ammonium sulphate to 30% saturation is gradually raised during two hours to a temperature of 60°. After the removal of the precipitated euglobulin, the ammonium sulphate is brought to 50% saturation and the resulting precipitate of ψ-globulin and antitoxin filtered, pressed, and dialysed. The advantages claimed by Banzhaf for the new process are, however, sometimes vitiated by the fact that the final product cannot be filtered except after long keeping, owing to the presence of an opalescent suspension presumably of euglobulin. By his original "two fraction" method, a clear filtrate is readily obtained.

The author now finds that an easily filterable end-product can be readily obtained by the following modification in the treatment, which causes an aggregation of the euglobulin into particles sufficiently large to admit of separation by filtration without any conversion of ψ-globulin into euglobulin. The serum or plasma is diluted with one-half its volume of water and ammonium sulphate added to 30% saturation, together with 1·5% of solid sodium chloride. The temperature of the mixture is gradually raised to 61°, 63°, or even 65°, and kept at this point for a few minutes only. The mixture is allowed to cool to 40° and filtered. The filtrate is then brought to 50% saturation with ammonium sulphate and subsequently treated as above described. It is considered that the shorter period of heating minimises the denaturation of the ψ-globulin (and consequent loss of antitoxic units) which otherwise occurs, and that the beneficial influence exerted by sodium chloride in the filtration processes is due to the adjustment of the hydrogen-ion concentration of the serum mixtures. H. W. B.

The Influence of Salicylate on Metabolism in Man. W. DENIS and J. H. MEANS (*J. Pharm. exp. Ther.*, 1916, **8**, 273—283).—In the case of two normal men the administration of large doses of sodium salicylate (up to 6·6 grams per day) produced an increase in the excretion of nitrogen, phosphates and uric acid. In one case the increased nitrogenous metabolism was accompanied by an increase in the basal metabolism, with symptoms of salicylate intoxication, whereas in the other case, with a greater increase in the urinary excretion of nitrogen, there was no increase in the basal metabolism and no symptoms of poisoning. Similar results to the latter case were obtained with a mildly septic individual. No change in the respiratory quotient was found in any of these cases. S. B. S.

Influence of the Nature of the Diet on the Retention of Protein. NOBUYOSHI UMEDA (*Biochem. J.*, 1916, **10**, 245—253).—The results of feeding experiments on dogs indicate that nitrogen in the form of protein added to a carbohydrate diet is retained in greater amount than when added to a fat diet of equal caloric value. The type of protein is of considerable importance; the addi-

tion of caseinogen leads to a greater nitrogen retention than is achieved by the addition of gelatin to the diet. The addition of meat extract to the gelatin does not increase the amount of nitrogen retained. H. W. B.

Some Reactions of Blood-vessels to Certain Chemicals. I. ADLER (*J. Pharm. exp. Ther.*, 1916, **8**, 297—324).—An account in some detail is given of observations of the action of alkalis, acids, and salts on the blood vessels of the mesentery of frogs. Alkalis cause a constriction, but the action of acids is not so definite, leading sometimes to dilatation, which is followed by constriction. S. B. S.

Nitrogen Distribution in the Tissues and some of the Factors which Influence it. GERTRUDE DORMAN CATHCART (*Biochem. J.*, 1916, **10**, 197—244).—The author has estimated the nitrogen distribution in the liver and muscle of normal dogs and of dogs which have received intravenous injections of sodium chloride, ammonia, glycine, and urea. The chief quantities estimated were: (i) dry matter, (ii) total nitrogen, (iii) protein nitrogen, (iv) non-protein nitrogen, (v) amino-acid nitrogen, (vi) amide nitrogen, (vii) ammonia nitrogen in 100 grams of the fresh tissue and the total and protein nitrogen in the dried tissue. Considerable differences occur between the values obtained for each tissue.

The intravenous injection of ammonia, urea, and glycine produces an accumulation of these substances as such in the liver and to a less extent in the muscle. Apparently a transformation of these accumulated small molecular substances into protein did not occur under the conditions of the experiments. Evidence was obtained of their further metabolism, particularly in the liver, of the following nature: ammonia is converted into amide nitrogen in both liver and muscle, indicating the formation of urea; urea is de-aminised in the liver and muscle, whilst glycine is de-aminised in the liver and is partly converted into urea in both liver and muscle. H. W. B.

The Osmotic and Colloidal Properties of Muscle. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1916, **75**, 48—70).—By investigation of the action of solutions on muscles in which the tissue structure has been destroyed, the author claims to have found a method by means of which he can distinguish between what he terms the osmotic and colloidal properties. As a result of investigations with muscle paste the conclusion is drawn that the change of weight in anisotonic solutions of sodium chloride are of purely osmotic character, whereas in salt solutions the increase of weight is partly of osmotic and partly of colloidal nature. The "colloidal" imbibition due to acids can be inhibited by the presence of salts. The imbibition due to acids of muscles is analogous to that shown by unorganised colloids, such as fibrin or gelatin. Coagulated muscular tissue shows a greater capacity for taking up water than does the uncoagulated. For this reason death rigor cannot be ascribed to a giving

up of water. A method is described for the measurement of permeability of tissue, both to salts and water. A cylinder of about 2 c.c. capacity is filled with a solution and covered at each end with a circular piece of the abdominal muscle of female frogs, and this is then immersed in various solutions. By determining the change of weight of the cylinder contents, and by analysis of the solution in the cylinder before and after the experiment, the movement of water or salt across the membrane can be ascertained. The permeability of normal tissue for sodium chloride was found to be extremely small, but on keeping the tissue it increases, and finally allows a free passage of the salt. Coagulation of the muscle also destroys its "semipermeability." S. B. S.

Narcosis. IV. Narcosis and Permeability. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1916, **75**, 71—100).—The method of investigation employed was that described by the author in his paper on the osmotic properties of muscles. Salt solutions (with or without narcotics) were enclosed in small cylinders closed by the tissue at each end and immersed in salt solutions containing the narcotic in the same concentration as that in the cylinder. By weighing and analysing the contents of the tubes before and after the experiment the influence of the narcotic on the permeability could be determined. In lower concentrations (sufficient, however, for the production of narcosis) the tissues undergo a decrease of permeability, which is reversible, that is, on allowing the tissue to remain in isotonic solutions without narcotics after the experiment, the permeability diminishes. In higher concentrations of the narcotics, however, the permeability of the tissue increases, and this change is an irreversible one. On these data a theory of narcosis is founded, which is similar to that propounded by Lillie, McClendon, Höber, and others. S. B. S.

The Physical and Chemical Processes taking place in Surviving Muscular Tissue, considered as the Causes of Death Rigor. LEONHARD WACKER (*Biochem. Zeitsch.*, 1916, **75**, 101—131). —The chief chemical processes, degradation of glycogen, formation and neutralisation of acid, take place within five to six hours of death, during which rigor sets in, and may be ascribed to these processes. In neutralisation of the acid, diphosphate is converted into monophosphate, carbon dioxide is set free from acid carbonates, and a protein is set free from an alkali albuminate. The following physical causes may be held responsible for the rigor: (*a*) An increase in the osmotic pressure in the tissue due to the degradation of glycogen to lactic acid; (*b*) increase of pressure due to liberation of carbon dioxide from the acid carbonate; (*c*) separation of protein from the alkali albuminate. The post mortem evolution of heat is due to the process of neutralisation.

The physiological processes may be summarised as follows: The quantity of acid formed depends on the alkalescence of the tissues. Accumulation of acid in the tissue tends to stop further degradation of the glycogen, and the appearance of free lactic acid is itself

prevented by the presence of alkali carbonate, diphosphate, and albuminate which react with lactic acid to form alkali lactate. The end-product of combustion of carbohydrates is not carbon dioxide, but carbonate of an alkali metal, due to oxidation of the lactate. Carbon dioxide itself is formed by the action of lactic acid on the carbonate. By means of the alkali carbonate of the blood, the alkalescence of the tissue is reconstituted after recovery. The alkali of the muscle can act at the same time as automatic regulators of the carbon dioxide pressure by means of the two following reversible chemical processes:

(*a*) $K_2HPO_4 + CO_2 + H_2O = KH_2PO_4 + KHCO_3$.

(*b*) $AlbNa + CO_2 + H_2O = AlbH + NaHCO_3$,

where Alb = protein component of the alkali albuminate. In case of overstraining of the muscle and of orthostatic albuminurea, the protein excreted in the urine has the same properties as the albuminate protein component of the muscle. S. B. S.

The Relation of Excised Muscle to Acids, Salts, and Bases. DOROTHY JORDAN LLOYD (*Proc. Roy. Soc.*, [B], **89**, 277—290).—Acids and alkalis both cause swelling of excised muscle, but the degree of swelling is not proportional to the strength, reaching its maximum in the cases of both hydrochloric acid and sodium hydroxide in the concentration of $0{\cdot}005N$. Alkalis first coagulate and then dissolve the muscle substance. Chlorides of the alkalis and alkaline earths all ultimately coagulate muscle in isotonic solutions, the salts containing bivalent cations acting more rapidly than those containing the univalent cations. The isoelectric point for muscle lies between $p_H = 5$ and $p_H = 7$. The swelling and shrinking of the tissue are ascribed to osmotic phenomena, which may be explained without assuming the presence of a semipermeable membrane round the fibres. S. B. S.

Precursor of Creatine in Chick Muscle. DAVID BURNS (*Biochem. J.*, 1916, **10**, 263—279).—The author has estimated the amount of guanidine in fertile eggs after increasing periods of incubation. The contents of the egg after extraction with ether are hydrolysed with 25% sulphuric acid, and then, after neutralisation, are oxidised by boiling calcium permanganate. The precipitated manganese hydroxide is filtered off, the excess of calcium removed by sodium carbonate, and the guanidine in the concentrated solution precipitated as picrate, which, after washing with water and ether, is dried and weighed.

In the developing chick embryo there is a regular increase in the guanidine content until the twelfth day of incubation. Thereafter there is a marked decrease, followed by a period of oscillation, and, finally, a slight but steady rise. It appears, therefore, that guanidine is continuously formed until the period at which, according to Mellanby (A., 1908, ii, 308), creatine first becomes recognisable in the incubating egg. The significance of the subsequent variation in the guanidine content has not been elucidated. H. W. B.

Thorium. A New Agent for Pyelography. J. EDWARD BURNS (*Bull. of the Johns Hopkins Hospital*, 1916, **27**, 157).—A 50% solution of thorium nitrate is used in the *X*-ray examination of the bladder. G. B.

The Chemical Constitution and Pharmacological Action of Substances of the Digitalis Group. WALTHER STRAUB (*Biochem. Zeitsch.*, 1916, **25**, 132—144).—The lethal doses of the various digitalis glucosides and their "genins" on frogs was determined, and also their relative actions in certain cases on the isolated hearts. The lethal doses are given in the following table, the results being expressed in grams of drug per gram of body-weight:

				Ratio glucoside "genin."
Digitoxin	0·0000036	Digitoxigenin	0·000006	2 : 7
K. strophanthin	0·00000075	Strophanthidin	0·0000025	3 : 1
Cymarin	0·0000008	Cymarigenin	0·0000025	3 : 1

Digitalin and digitalenin were not sufficiently soluble for determinations of toxicity to be made. The glucosides are therefore more toxic than their genins. The toxicities of cymarin, cymarigenin, and cymaric acid, of which the chemical relationships to one another were determined by Windaus, were found to be 0·0000008, 0·0000025, and 0·00042 (in the same units). The benzoate of cymarigenin (which is identical with strophanthidin) has a smaller toxicity, represented by the number 0·000025. No conclusions can be drawn as to the relationship between chemical constitution and pharmacological action. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Use of Ammonia in the Chlorination of Water. J. RACE (*Pharm. J.*, 1916, **97**, 85; from *Lancet*, 1916, 71).—The germicidal value of ammonium hypochlorite is twenty to thirty times as great as that of an equivalent amount of the calcium salt, and surpasses also that of the sodium and potassium salts. It is probable that this is to be ascribed to its instability in dilute solution, chloroamine being formed according to the equation: $NH_4OCl = NH_2Cl + H_2O$, which substance, as is well known, has a much greater germicidal action than the equivalent quantity of chlorine. The ammonium hypochlorite solutions were prepared by the double decomposition of calcium hypochlorite and ammonium oxalate, the precipitate being removed by centrifugation. Dilute solutions of chloroamine having the same efficiency were obtained by the addition of ammonia to calcium hypochlorite solutions. A noteworthy feature of the treatment of water with hypochlorite and ammonia

was the almost entire absence of absorption. When hypochlorite alone was added to Ottawa River water, 35% of the available chlorine content of 10 parts per million was absorbed in five minutes at 15°, and 60% within an hour. When, however, an equivalent of ammonia is added, only 1·4% of the available chlorine is absorbed in an hour, and 3·2% in twenty hours. G. F. M.

Velocity of Decomposition of Lactose by the "Bulgarian Ferment." I. G. QUAGLIARIELLO and C. VENTURA (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 751—757).—The rate at which lactose is converted into lactic acid by *Bacillus bulgaricus* in milk, whey, and a solution of lactose in Ringer's solution containing 1% of peptone, in all cases at 38°, has been measured. The results are given in the form of curves and tables. T. H. P.

The Gases of Swamp Rice Soils. III. A Hydrogen Oxidising Bacterium from these Soils. W. H. HARRISON and P. A. SUBRAMANIA AIYER (*Mem. Dept. Agric. India Chem. Ser.*, 1916, **4**, 135—148. Compare A., 1915, i, 202).—Two organisms were isolated from the organised soil film, a hydrogen oxidising bacterium designated H_A, and a motile bacterium, H_B. The bacterium H_A is non-motile, and is quite different from Kaserer's organism, *B. pantotropus*. It does not grow well in mineral solutions or on solid mineral media under autotropic conditions in presence of carbon dioxide, methane, hydrogen, and oxygen. Whilst under these conditions it is practically inactive, it readily oxidises hydrogen when associated with H_B and water bacteria. On all ordinary organic nutrient media the organism H_A grows well, and under these conditions oxidises hydrogen, the intensity of the oxidation depending on the kind and amount of organic matter present. With large amounts of organic matter the oxidation of hydrogen reaches a minimum. The best results are obtained with 0·01—0·03% of peptone, sodium aspartate, etc. Prolonged cultivation on organic media results in the total loss of oxidising power.

When ammonia and dextrose are employed as sources of nitrogen and carbon, the organism H_A oxidises a fair amount of hydrogen, and produces a considerable amount of carbon dioxide from the dextrose; with a nitrate as source of nitrogen, the growth was fairly good; only a small amount of hydrogen was oxidised, and there was no production of nitrite. N. H. J. M.

Influence of Catalysts (Alkaloids and Dyes, etc.) on Yeast Fermentation. R. SOMOGYI (*Int. Zeitsch. phys.-chem. Biol.*, 1916, **2**, 416—429).—Small amounts of quinine and atropine accelerate the growth of yeast, whilst larger quantities inhibit it. With cocaine and pilocarpine, on the contrary, small amounts inhibit whilst larger quantities have an accelerating influence on the fermentation (compare Traube and Onodera, A., 1915, ii, 92).

Basic dyes, such as malachite-green and methylene-blue, exert a toxic action on the yeast-cells when present in moderate concentration. When, however, only a trace of methylene-blue is added, the

activity of the yeast appears to be enhanced and fermentation is accelerated.

Most of the acid dyes examined did not materially influence the rate of fermentation even when present in considerable amounts.
H. W. B.

Decomposition of Lactic Acid by Killed Yeast. V. I. PALLADIN and D. SABININ (*Biochem. J.*, 1916, **10**, 183—196).—The first stage of alcoholic fermentation is regarded as consisting of a series of oxidations and reductions at the expense of water, resulting in the formation of organic acids, which subsequently undergo anærobic oxidation in which reductase participates by transferring hydrogen from one compound (reductor) to another (hydrogen acceptor) (compare A., 1914, i, 1036). In agreement with this supposition it is found that lactic acid, when digested with hefanol in the presence of methylene-blue (M), yields equivalent amounts of acetaldehyde and carbon dioxide according to the equation:

$$CH_3\cdot CH(OH)\cdot CO_2H + M = CH_3\cdot CHO + CO_2 + MH_2.$$

Since the reduced methylene-blue is readily oxidised by atmospheric oxygen, methylene-blue behaves in this connexion like a respiratory pigment.

Pyruvic acid itself may act as the hydrogen acceptor, thus, $OH\cdot CHMe\cdot CO_2H + COMe\cdot CO_2H = CHMeO + CO_2 + OH\cdot CHMe\cdot CO_2H$; $OH\cdot CHMe\cdot CO_2H + CHMeO = COMe\cdot CO_2H + CH_2Me\cdot OH$, and in accordance with this view it is found that the addition of pyruvic acid to a digestion mixture of killed yeast and lactic acid leads to a greater evolution of carbon dioxide and the simultaneous production of a small amount of alcohol. Alcohol is not produced when lactic acid, methylene-blue, and killed yeast are digested in the absence of pyruvic acid.
H. W. B.

Phytobiochemical Studies. I. AS. ZLATAROFF (*Biochem. Zeitsch.*, 1916, **75**, 200—210).—Analyses of the seeds of *Cicer arietinum* after varying periods of germination in distilled water. These refer to the water and ash content, and to the various constituents containing nitrogen and phosphorus. After twenty-five days' germination the protein content sinks to about one-third of its original value, whilst the nuclein content remains almost unchanged. The ammonia nitrogen is very small. The inorganic phosphorus increases at the cost of the protein phosphorus compounds and of the more soluble organic phosphorus compounds. Phytin appears to act, therefore, chiefly as a reserve substance, as do the protein phosphorus compounds. Lecithin does not diminish to the same extent during germination, and does not therefore act apparently exclusively as a reserve substance. When added in emulsion form it promotes the growth of the seedlings of *Cicer arietinum* in the presence of light.
S. B. S.

Algerita Root. MERRILL C. HART (*Amer. J. Pharm.*, 1916, **88**, 301—302).—The algerita plant (*Odostemon trifoliatus*, *Berberis trifoliatus*) grows most abundantly in Texas and New Mexico, and

infusions of the root are used as a remedy for sore eyes and mouths, etc. The root was found to contain 1·49% of berberine and about 0·1% of other alkaloids; hydrastine was not present. W. P. S.

Principle Extracted from Amatscha. H. MANIWA (*J. Pharm. Chim.*, 1916, [vii], **14**, 55—56; from *Yakugakuzasshi*, 1915).—The leaves of amatscha (*Hydrangea Tunbergii*) contain a sweet *substance* having the formula $C_{16}H_{14}O_5$ and melting at 128°; it yields a *diacetyl* derivative, m. p. 144°, and a *dibenzoyl* derivative, m. p. 162°. It gives a violet coloration with ferric chloride, and is soluble in sodium hydroxide solution; it has the properties of a lactone. When fused with potassium hydroxide, the substance yields pyrocatechuic acid and a homosalicylic acid, m. p. 168°. W. P. S.

Composition of the Fruit of Evodia Rutaecarpa. Y. ASAHINA and K. KASHIWAKI (*J. Pharm. Chim.*, 1916, [vii], **14**, 54—55; from *Yakugakuzasshi*, 1915. Compare this vol., i, 238).—The fruits contain a terpene, *evodene*, which readily oxidises and resinifies. Two alkaloids have also been isolated from the fruits. One of these, *evodiamine*, $C_{19}H_{17}ON_3$, m. p. 278°, is insoluble in water, benzene, and light petroleum, slightly soluble in cold alcohol, ether, ethyl acetate, and chloroform, and soluble in acetone. It gives an orange-yellow coloration with sulphuric acid, the colour changing to reddish-brown and then to blue after some time or on dilution with water. A similar range of colours is obtained when the substance is dissolved in hydrochloric acid. When heated with alcohol and hydrochloric acid it is converted into iso*evodiamine*, m. p. 155—156°. The other alkaloid, *rutaecarpine*, $C_{18}H_{13}ON_3$, m. p. 258°, crystallises in small, yellow plates. It is slightly more soluble in the various solvents than is evodiamine. W. P. S.

An Explanation of the Laxative Action of White Mustard Seed. E. C. VAN LEERSUM (*J. Pharm. exp. Ther.*, 1916, **8**, 285—296). —The laxative action is ascribed to the setting free of hydrogen sulphide from the seeds. The amount evolved by warming the seeds with water at 37° was estimated. S. B. S.

The Presence of Phycoerythrin in Nostoc commune. E. TEODORESCO (*Compt. rend.*, 1916, **163**, 62—64).—The author has extracted specimens of *Nostoc commune*, grown under somewhat abnormal conditions so that the blue pigment was not produced, with chloroform water, and shown the presence of phycoerythrin in the extract by the identity of its band spectrum with that of an extract of *Ceramium rubrum*, which is known to contain this pigment. W. G.

Chemical Composition of Oscillaria prolifica. B. B. TURNER (*J. Amer. Chem. Soc.*, 1916, **38**, 1402—1410).—The study of *Oscillaria prolifica* was undertaken owing to the fact that this and similar algæ have caused considerable trouble in connexion with the water supplies of Massachusetts. The air-dried material con-

tained 9·7% of moisture, 46·25% of proteins, and a small quantity of fat, and yielded 6·4% of ash. A small amount of a crystalline magnesium salt of an organic acid (probably hexoic acid) was isolated, and evidence was obtained of the presence of a glucoside or polysaccharide with physical properties resembling those of saponin. Various colouring matters from the alga have been examined spectroscopically, including a chlorophyll, similar to that of the higher plants, and a blue substance with an intense red fluorescence, which is regarded as new and is termed *algocyan*. The principal carbohydrate is a pectin-like substance which is slowly hydrolysed by 5% sulphuric acid with production of a non-reducing substance with a high positive rotation and a reducing sugar with a smaller rotation.

The unpleasant odour and taste of the decaying alga is due chiefly to higher fatty acids of the butyric series and traces of indole and scatole. The fresh alga contains an aromatic compound, soluble in light petroleum.

A modified Kjeldahl method is described for the analysis of very small quantities (5—10 mg.) of material containing 1 mg. or less of nitrogen. E. G.

Poisonous Principle of Poison Oak (Rhus diversiloba, T. and G.). JAMES B. MCNAIR (*J. Amer. Chem. Soc.*, 1916, **38**, 1417—1421).—*Rhus diversiloba*, the poison-oak, is very similar in appearance to *R. toxicodendron*, the poison ivy, the chief difference between them being in the form of their leaflets. The former plant has not hitherto been studied chemically, but the latter has been examined by Acree and Syme (A., 1906, ii, 795), who stated that the poisonous constituent is a glucoside of fisetin, rhamnose and gallic acid.

The branches or leaves of *R. diversiloba* on extraction with gasolene yielded a black substance, which was thoroughly extracted with water and subsequently with 95% alcohol. The aqueous solution was found to be non-poisonous, but the alcoholic extract was poisonous. Further examination of the poisonous material proved that it is not a glucoside of fisetin, rhamnose, and gallic acid, as none of these substances was produced on hydrolysis. In view of the close relationship between *R. toxicodendron* and *R. diversiloba*, it is suggested that the examination of the former plant should be repeated, and it is pointed out that fisetin, rhamnose, and gallic acid are found in two non-poisonous species of Rhus, and that the natural glucoside of these substances is non-toxic. E. G.

Constituents of Poison Ivy (Rhus toxicodendron). S. F. ACREE (*J. Amer. Chem. Soc.*, 1916, **38**, 1421—1425).—A reply to the criticisms of McNair (preceding abstract) on the work of Acree and Syme (A., 1906, ii, 795). E. G.

Comparative Experiments on the Utilisation of Nitrogen and Phosphoric Acid by Plants. TH. PFEIFFER and W. SIMMERMACHER (*Landw. Versuchs-Stat.*, 1916, **88**, 445—463).—Pot experiments in which oats were grown in glass sand manured with the

usual minerals and with increasing amounts of nitrogen and of phosphoric acid in the forms of ammonium nitrate and hydrogen calcium phosphate respectively.

The utilisation of phosphoric acid in percentages of the amounts employed showed an increase from the first to the second amount, and then a fall; whilst with nitrogen the percentage increased from the lowest to the highest.

Comparing the nitrogen and phosphoric acid results, it is shown that the average percentage of nitrogen utilised was 83·8, whilst that of the phosphoric acid was 71·4. N. H. J. M.

Bleaching of Flour by Nitrogen Peroxide. K. Scheringa (*Chem. Weekblad*, 1916, **13**, 840—849; *Pharm. Weekblad*, 1916, **53**, 945—954).—Flour bleached with nitrogen peroxide is always contaminated with nitrites. From a dietetic point of view the author regards the presence of these substances as by no means innocuous. A. J. W.

Is the Use of Flour Bleached with Hydrogen Peroxide Injurious to Health? F. A. Steensma (*Chem. Weekblad*, 1916, **13**, 849—854; *Pharm. Weekblad*, 1916, **53**, 955—960. Compare preceding abstract).—The author considers that the proportion of nitrites introduced into flour by bleaching with nitrogen peroxide is too small to cause any injury to health. A. J. W.

Non-protein Nitrogenous Constituents of Feeding Stuffs. H. S. Grindley and H. C. Eckstein (*J. Amer. Chem. Soc.*, 1916, **38**, 1425—1431).—In order to prove the accuracy of the application of van Slyke's method of estimating the different amino-acids of proteins to the estimation of the free and combined amino-acids and the free and combined amides of feeding stuffs, it was necessary to prove that the non-protein nitrogenous constituents do not vitiate the results, and the present work was therefore undertaken.

The non-protein nitrogenous constituents of lucerne hay, timothy hay, blood meal, maize, and clover hay have been estimated, the separation of the proteins from the non-proteins being effected by means of colloidal ferric hydroxide. The results show that the non-protein constituents consist largely of the forms of nitrogen which are produced by the hydrolytic decomposition of proteins, the sum of the amide nitrogen, humic nitrogen, free and combined amino-acid nitrogen, and the free and combined acid amide nitrogen representing from 80%, in the case of lucerne hay, to 94%, in the case of blood meal, of the non-protein nitrogen. Of the soluble nitrogen, not precipitated by colloidal ferric hydroxide, the humic nitrogen constituted from 53 to 63%, the free and combined acid amide nitrogen from 17·11% to 25·67%, and the ammonia nitrogen from 6·33% to 12·04%. E. G.

Transformation of Carbohydrates in Sweet Potatoes. Heinrich Hasselbring and Lon A. Hawkins (*Chem. Zentr.*, 1916, i, 618; from *J. Agric. Research*, 1915, **5**, 543—560).—The sugar

content of sweet potatoes (*Ipomoea batatas*) remains comparatively low until after they have been harvested. The change of the starch into sugar is not particularly influenced by the temperature, but seems to be dependent on internal circumstances, and is apparently connected with the cessation of the activity of the leaves, as, if the stem is cut off and the supply of food material to the tubers thereby stopped, the starch transformation which was previously in abeyance at once begins, even if the tubers are left in the ground. The transformation of the starch in the stored potatoes results apparently first in the production of reducing sugars, which are then converted into sucrose. The reaction proceeds at first rapidly at high temperatures, but soon becomes slower and approaches an end-point; at lower temperatures the change is slower, and the end-point alters to such an extent that a great accumulation of sugar can be formed. G. F. M.

Chemical Actions in the Subsoil of the Dunes. J. Versluys (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1619—1624).—A discussion of the changes which take place in the subsoil of the dunes whereby the calcium and magnesium of fresh water are replaced by sodium.

Analytical data show that the content of sodium + calcium + magnesium in the transparent fresh water is not greater than that of the original fresh water. On the other hand, the ratio of sodium to sodium + calcium + magnesium is not only very much greater than in the fresh water, but is also somewhat greater than in sea-water. It is suggested that the observed changes in composition are due to the interaction of the fresh water with substances present in the subsoil which are similar to the artificial zeolites of Gans.

H. M. D.

Organic Chemistry.

Thermal Decomposition of the Propane-Butane Fraction from Natural Gas Condensate. J. E. ZANETTI (*J. Ind. Eng. Chem.*, 1916, **8**, 674—678).—Mixtures of propane and butane are decomposed at high temperatures, yielding ethylene, butene, and lower unsaturated substances, hydrogen, and aromatic substances. The proportion of unsaturated substances increases to a maximum as the temperature rises to about 750°, and then decreases as the temperature increases. The proportion of hydrogen formed increases with an increase of the temperature. The formation of aromatic substances begins at about 750°, and is coincident with an increase in the rate of the production of hydrogen. The catalytic action of copper, iron, and nickel was investigated; iron and nickel were found to prevent the formation of aromatic substances and to favour the decomposition of the hydrocarbons into free carbon and hydrogen. It was also found that the tar "fog" in the gases resulting from decomposition of hydrocarbons at high temperatures could be condensed by passing the gases between copper plates connected with an induction coil capable of giving a 2-inch spark.

W. P. S.

Polymerisation of Ethylene. G. DE MONTMOLLIN (*Bull. Soc. chim.*, 1916, [iv], **19**, 242—247. Compare Ipatieff, A., 1911, i, 937). —An examination of the oily layer which collects on the surface of the water in the cooled receiver in Newth's process for the preparation of ethylene (T., 1901, **79**, 915). The author has prepared a large quantity of this oil, of which 6·2 grams are obtained for every 100 c.c. of alcohol used, and by means of a long series of fractional distillations has isolated from it the following hydrocarbons: di*iso*propyl, $\gamma\gamma$-dimethylpentane, 1 : 3-dimethyl*cyclo*hexane, 1 : 4-dimethyl*cyclo*hexane, *iso*propyl*cyclo*hexane, a mixture of 1-methyl-4-*iso*propyl*cyclo*hexane and decanaphthene, and a mixture of dodecanaphthene and tetradecanaphthene. The reaction which occurs is rather one of condensation than of polymerisation.

W. G.

Preparation of Methyl Chloride from Methane. A. HOCHSTETTER (D.R.-P., 292089; from *J. Soc. Chem. Ind.*, 1916, **35**, 867). —Methyl chloride is obtained from methane by the action of carbonyl chloride at high temperatures according to the equation: $CH_4 + COCl_2 = CH_3Cl + CO + HCl$. The reaction is brought about by leading the gases, which should contain a slight excess of methane, over a catalyst capable of acting as a chlorine carrier or of accelerating the reaction by surface condensation. G. F. M.

Colloidal Carbon, and the Decomposition of Organic Liquids by the Electric Arc. STANISLAW TARCZYNSKI (*Zeitsch. Elektrochem.*, 1916, **22**, 252—254).—The action of a direct current arc (110 volts,

8—10 amperes) on chloroform and carbon tetrachloride has been investigated. The arc was completely immersed in the liquid, and the action carried out in the way adopted for the production of colloidal metals (Bredig). In the case of carbon tetrachloride, quantities of carbon and chlorine separated during the reaction. After filtration, a brown or olive-green solution remained, which exhibited all the characteristics of a colloidal solution, and on warming deposited amorphous carbon. On fractionation, the liquid was shown to consist of a carbon tetrachloride solution of hexachloroethane, tetrachloroethylene, and hexachlorobenzene. In the case of chloroform there was the same deposition of carbon and production of a colloidal solution of carbon with evolution of hydrogen chloride. The filtered solution contained carbon tetrachloride, tetrachloroethylene, *s*-tetrachloroethane, pentachloroethane, hexachloroethane, and hexachlorobenzene. In the present experiments, which are to be regarded as preliminary, the quantity of hexachlorobenzene produced was relatively very large in comparison with the quantities of the other products. J. F. S.

The Organomagnesium Derivative of αε-Dichloropentane. ENRIQUE V. ZAPPI (*Bull. Soc. chim.*, 1916, [iv], **19**, 247—251).—Following the method used by Braun and Sobecki (compare A., 1911, i, 701) for studying the magnesium derivatives formed from αε-dibromopentane, the author has prepared the magnesium derivative from αε-dichloropentane, decomposed the mixture with water, and weighed the hydrocarbons formed. The results show that in the preparation of the magnesium derivative, 86·9% of the dichloropentane reacted normally, 5·9% reacted forming a chain of ten carbon atoms, and the remainder gave more highly condensed compounds. There was no indication of the formation of *cyclo*pentane. W. G.

Conversion of Aliphatic Nitrites into Nitro-compounds. PAÑCHĀNAN NEOGI and TĀRINCHARAN CHOWDHURI (T., 1916, **109**, 701—707. Compare Neogi, T., 1914, **105**, 2371).—An investigation of the conditions under which the aliphatic nitrites can be converted into nitro-compounds.

It is found that aliphatic nitrites can be partly converted into the corresponding nitro-compounds by passage in the form of vapour through a heated glass tube filled with asbestos wool. The simplest behaviour was observed with methyl and ethyl nitrites, which first showed signs of conversion at 100°, the optimum temperature being 120—130°. At higher temperatures decomposition occurred with formation of the corresponding aldehyde and acid. With *iso*propyl nitrite, *n*-propyl nitrite, *iso*butyl nitrite, and *iso*amyl nitrite the same conversion into the corresponding nitro-compound was observable, although with increasing molecular weight the decomposition giving aldehyde and acid became more marked. The presence of traces of moisture appears to facilitate the conversion of the nitrite into the nitro-compound, but with a larger quantity of water the formation of the alcohol, aldehyde, and acid occurred much more rapidly. These results provide an explanation of the observation

of Gaudion (A., 1912, i, 163) that on passing a mixture of hydrogen and aliphatic nitrite over heated nickel powder, an amine is produced, the change being dependent on the primary formation of the nitro-compound.

Judging from the slight extent of the conversion of nitrite into nitro-compound at 100°, it is apparent that the production of nitro-compounds in the interaction of alkyl iodides and mercury or silver nitrites cannot be due to this cause, and the conclusion is drawn that in such interactions to some extent unstable intermediate products are obtained, the decomposition of which yields the nitro-compound, whilst the direct double decomposition of the reagents gives the aliphatic nitrite. D. F. T.

Trimethyl- and Triethyl-sulphonium Nitrites. CHARLES WESLEY ADDY and ALEXANDER KILLEN MACBETH (T., 1916, **109**, 755—757).—In a former paper (T., 1915, **107**, 87) the authors assumed the existence of colourless final additive products from mixing alkyl sulphides with organic nitrites. This has now been confirmed by the isolation of two such products. A sulphonium iodide was triturated with silver nitrite in the presence of a small quantity of water. The solution was filtered, cooled to 0°, and again filtered, the filtrate being further concentrated in a vacuum. In this way *trimethyl-* and *triethyl-sulphonium nitrites* were obtained as flat, colourless plates. The former, when heated in a vacuum, melted and decomposed at 92—93°, giving off methyl sulphide, methyl nitrite, and nitric oxide, and leaving a brown, syrupy residue which responded to tests for nitrates. The latter, when similarly heated, melted and decomposed at 95°, giving off ethyl sulphide, ethyl nitrite, and nitric oxide, and leaving a brown residue which responded to tests for nitrates. W. G.

Auto-oxidisable Substances and Systems of Physiological Interest. IV. Catalytic Acceleration by Potassium Dichromate of Oxygen Absorption by Lecithin. TORSTEN THUNBERG (*Skand. Arch. Physiol.*, 1916, **33**, 228—230. Compare A., 1913, i, 1041; 1914, i, 386).—0·0001 Molar dichromate more than doubles and 0·001 molar more than quadruples the absorption.

Unsaturated acids are similarly affected. The author considers this the reason why chromic acid is found useful in histology. G. B.

Compounds of Quinquevalent Molybdenum. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 775—782).—The author has investigated the interaction of hydrated molybdenum pentoxide with formic or oxalic acid, and has discovered a series of double salts containing, not the radicle molybdenyl, $Mo^{V}O$, but the new univalent radicle, $Mo^{V}O_2$, for which the name *molybdyl* is suggested. This radicle is analogous to the vanadium radicle, $V^{V}O_2$, contained in various compounds of vanadic acid with hydrofluoric, oxalic, and citric acids (compare A., 1915, i, 497), and is isomeric with the radicle, $Mo^{VI}O_2$, found in certain derivatives of molybdic anhydride,

for instance, $Mo^{VI}O_2F_2,2KF$. The new salts now described are of the three types: $Mo^{V}O_2X,RX$; $Mo^{V}O_2X,2RX$; and $2Mo^{V}O_2X,3RX$.

Ammonium molybdyl formate, $2H\cdot CO_2MoO_2,3H\cdot CO_2NH_4$, forms transparent, orange-red, tabular crystals of hexagonal shape; in absence of formic acid, its aqueous solution deposits, slowly in the cold but rapidly on heating, a yellow, amorphous compound, which is probably a basic salt.

Analogous compounds which have been prepared are: *potassium molybdyl formate*, $2H\cdot CO_2MoO_2,3H\cdot CO_2K$, rose-red needles; *sodium molybdyl hexamethylenetetramine formate*,

$$2H\cdot CO_2MoO_2,2(H\cdot CO_2H,C_6H_{12}N_4),H\cdot CO_2Na,$$

slender, red needles, and *molybdyl hexamethylenetetramine formate*, $H\cdot CO_2MoO_2,(H\cdot CO_2H,C_6H_{12}N_4),3H_2O$, orange-yellow needles, readily decomposed by water.

Quinquevalent molybdenum might be expected to be capable of giving oxalates richer in oxalic acid than Bailhache's compounds (A., 1903, i, 66), but the author could only obtain compounds of the type $2R_2O,Mo_2O_5,3C_2O_3,2H_2O$, R being either K or NH_4.

Ammonium molybdyl oxalate, $(MoO_2)_2C_2O_4,2(NH_4)_2C_2O_4,3H_2O$, forms shining, microscopic, cinnamon-coloured scales, and dissolves slowly in water with decomposition, and *potassium molybdyl oxalate*, $(MoO_2)_2C_2O_4,2K_2C_2O_4,2H_2O$, has similar appearance and properties.

According to Werner's nomenclature, ordinary molybdenyl salts are oxo-molybdanates, whereas the compounds described above are dioxo-molybdanates, molybdyl hexamethylenetetramine formate having the formula $\left[Mo{}^{O_2}_{(H\cdot CO_2)_2}\right]H,C_6H_{12}N_4,3H_2O$. The oxalates $(MoO_2)_2C_2O_4,2R_2C_2O_4,2H_2O$ evidently correspond with the type $\left[Mo{}^{O_2}_{X_3}\right]R_2$, doubled owing to the dibasicity of oxalic acid, and since the water in these compounds is not eliminated at 100°, it probably exists as hydroxyl, thus: $\left[\begin{matrix}O_2\\ Mo_2(OH)_4\\ (C_2O_4)_3\end{matrix}\right]R_4$. The double formates of the type $2H\cdot CO_2MoO_2,3H\cdot CO_2R$ may be formulated thus:

$$\left[Mo_2{}^{O_4}_{(H\cdot CO_2)_5}\right]R_3 \text{ or } \left[Mo{}^{O_2}_{(H\cdot CO_2)_3}\right]R_2 + \left[Mo{}^{O_2}_{(H\cdot CO_2)_2}\right]R.$$

T. H. P.

Fatty Oils in the Light of Mesomorphous Polymerisation. W. FAHRION (*Ber.*, 1916, **49**, 1194—1196. Compare Kronstein, this vol., i, 462).—The author has frequently criticised Kronstein's views (see *Farben-Zeit.*, 1912, 1913), and now attacks his last paper severely. It is asserted that the different drying capacities of oils must be due first and foremost to their chemical constitutions. Particularly wood oil owes its unique properties to the fact that it largely contains α-elæostearic acid, and castor oil to its ricinoleic acid, which are peculiar to these oils. J. C. W.

Potassium Uranyl Oxalates. A. COLANI (*Compt. rend.*, 1916, **163**, 123—125).—A study of the system water: uranyl oxalate: normal potassium oxalate at 15° and 50°. The results show the existence of an anhydrous salt, $K_2(UO_2)(C_2O_4)_2$, not yet isolated. The hydrate, $K_2(UO_2)(C_2O_4)_2,3H_2O$, is not formed at the ordinary temperature, but probably exists below 50°. There is a marked and immediate increase in the solubility of uranyl oxalate in potassium oxalate, this indicating the formation of molecular complexes, but in none of the combinations with potassium is the character of the uranyl radicle hidden. W. G.

Additive Products of Oxalic Acid. A. MADINAVEITIA and J. SOROLLA (*Anal. Fis. Quim.*, 1916, **14**, 298—305).—A description of the additive products formed by mixing oxalic acid and certain phenols in ether solution. Phenol gives a *compound*, $C_{14}H_{14}O_6$, tabular crystals, m. p. 126—127°; *p*-cresol, a *compound*, $C_{16}H_{18}O_6$, acicular laminæ, m. p. 124°; quinol, a *compound*, $C_8H_8O_6$, laminæ, m. p. 216° (decomp.); β-naphthol, a *compound*, $C_{22}H_{22}O_6$. Negative results were obtained with thymol, eugenol, α-naphthol, catechol, resorcinol, orcinol, pyrogallol, salicylic acid, *p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde, *p*-bromophenol, *o*-nitrophenol, *p*-nitrophenol, picric acid, methyl, ethyl, *iso*butyl, and amyl alcohols. A. J. W.

Vital Oxidation of Succinic Acid. TORSTEN THUNBERG (*Skand. Arch. Physiol.*, 1916, **33**, 223—227).—Succinates are oxidised by free oxygen in the presence of certain tissues, for example, minced muscle. The oxidation is stopped by sulphur and by hydrogen sulphide, but not when lead carbonate or lead oxide is also present. In such experiments contamination with vulcanised rubber must be avoided. G. B.

The Configuration of Muconic Acid. Synthesis of Mucic Acid. ROBERT BEHREND (*Ber.*, 1916, **49**, 999—1003).—Among the products of the oxidation of muconic acid by cold alkaline permanganate were identified formic, oxalic, mucic, racemic, but not mesotartaric acid. Muconic acid is therefore constituted like fumaric acid, and is represented by the formula,

$$\begin{array}{c} HC\text{———}CH \\ CO_2H\cdot\ddot{C}H \quad H\ddot{C}\cdot CO_2H \end{array}.$$

Idosaccharic acid was also to be expected, and it was indeed identified among the products when the oxidation was performed by means of sodium chlorate in the presence of a little osmium tetroxide (Hofmann, A., 1913, ii, 609). The chief product in this case, however, was mucic acid, which opens up the way to a complete synthesis of the galactose group of sugars. J. C. W.

Ester Acids of Lemon Juice. L. WOLFRUM and JOH. PINNOW (*Zeitsch. Nahr. Genussm.*, 1915, **30**, 144—156).—Ethyl citric acid [ethyl dihydrogen citrate] was separated from lemon juice by fractional extraction in a Partheil-Rose apparatus and precipita-

tion as its calcium salt. The same acid was prepared by boiling together alcohol and citric acid. The calcium, lead, and silver salts of the acid were obtained; these salts were soluble with difficulty. The specific gravity of aqueous solutions of the acid, and its distribution-coefficients at 15° and 27° between water and ether were determined, as well as its rate of extraction and rate of saponification. Ethyl citric acid saponifies very slowly. The presence of an anhydride of the acid was not detected. W. P. S.

Some Numerical Relations among the Rotatory Powers of the Compound Sugars. C. S. Hudson (*J. Amer. Chem. Soc.*, 1916, **38**, 1566—1575).—By the term "compound sugar" the author distinguishes the crystalline polysaccharides from their less definitely characterised relatives (starch, glycogen, cellulose, pentosans, etc.) and from monosaccharides.

The numerical relationships that have been found to hold among the rotatory powers of the α- and β-forms of the monosaccharides and their glucosidic derivatives (A., 1909, i, 135) are extended to several of the compound sugars. A relation is deduced by which it is shown that, for the sugars of the sucrose group (sucrose, raffinose, gentianose, stachyose) which are hydrolysed by invertase to yield lævulose and an aldose, the molecular rotation of the aldose is less than that of its parent sugar by 2340 for its α-form and 19,300 for its β-form. The rotatory powers of melibiose, gentiobiose, and manninotriose may be calculated by this relation.

The relation is applicable to sugars of the trehalose group and also to acetylated sugars.

By means of the relation it is shown that the common dextrose residues of lactose and cellose probably have identical structure.

C. S.

Isomeric α- and β-Hexa-acetates of α-Glucoheptose. C. S. Hudson and E. Yanovsky (*J. Amer. Chem. Soc.*, 1916, **38**, 1575—1577).—The β-hexa-acetate, obtained by heating anhydrous sodium acetate, α-glucoheptose, and acetic anhydride and repeatedly crystallising from 50% alcohol, has m. p. 135° and $[\alpha]_D^{20}$ +4·8° in chloroform. The α-hexa-acetate was prepared by heating the β-isomeride with acetic anhydride and a little zinc chloride and repeatedly crystallising the product from ether; it has m. p. 164° (Fischer records 156°), and $[\alpha]_D^{20}$ +87·0° in chloroform.

The difference between the molecular rotations of the two hexa-acetates (compare preceding abstract) is practically identical with that between the α- and β-penta-acetylglucoses, and there is thus good evidence that the two hexa-acetates constitute an α- and β-pair. Since α-glucoheptose is a derivative of *d*-glucose, its more dextrorotatory hexa-acetate is to be named the α-form, and the other, $[\alpha]_D^{20}$ +4·8°, the β-form. C. S.

Action of Light on Iodine and Starch Iodide in Aqueous Medium. H. Bordier (*Compt. rend.*, 1916, **163**, 205—206).—Solutions formed by adding either 10 drops of a 10% alcoholic solution of iodine to a litre of water, or 3 drops of the alcoholic

solution to a litre of water containing a little starch paste, are decolorised by exposure to sunlight for a few hours, although control solutions kept in the dark do not lose their colour. The solution containing the starch has its colour restored by the addition of a trace of iodine. Light which has passed through yellow glass also causes this decoloration, and the author suggests that this loss of colour is due to the conversion of the iodine into hydriodic acid under the influence of the light, this being borne out by the fact that the solutions have an acid reaction after the loss of colour. W. G.

Preparation of Derivatives of Hexamethylenetetramine. J. D. RIEDEL (D.R.-P., 292284; from *J. Soc. Chem. Ind.*, 1916, **35**, 867).—Hexamethylenetetramine forms an easily soluble non-deliquescent salt with perchloric acid, $C_6H_{12}N_4,HClO_4$, which is readily converted in aqueous solution into a dibromo- or di-iodo-derivative. These are stable, insoluble compounds, having a strong antiseptic action. G. F. M.

Synthesis of Hydroxy-bases and Homologous Cholines. J. VON BRAUN (*Ber.*, 1916, **49**, 966—977).—The bromoalkyl benzoates described in an earlier paper (A., 1913, i, 720) have been applied to the preparation of compounds of the type $R_2N\cdot[CH_2]_x\cdot OBz$, from which the amino-alcohols, $R_2N\cdot[CH_2]_x\cdot OH$, and finally homologous cholines, $NR_3Cl\cdot[CH_2]_x\cdot OH$, have been obtained. In the case of combinations in which $x=4$ or 5 and $R=CH_3$, it was found that the first ester tends to undergo rearrangement, even during its preparation, but especially on distillation, into the benzoate of a quaternary, cyclic base, thus: $R_2N\cdot[CH_2]_x\cdot OBz \longrightarrow OBz\cdot NR_2\colon[CH_2]_x$.

γ-Bromopropyl benzoate and dimethylamine are dissolved in benzene and heated for a few hours at 100°, when *γ-dimethylaminopropyl benzoate*, $NMe_2\cdot C_3H_6\cdot OBz$, is obtained in 90% yield as a colourless liquid, b. p. 159—160°/20 mm., which is hydrolysed to *dimethyl-γ-hydroxypropylamine*. This is a mobile liquid, b. p. 163—164°, with a very basic odour, and forms a *methiodide*, $NMe_3I\cdot C_3H_6\cdot OH$, m. p. 195°, which may be converted into γ-homocholine chloride by means of silver chloride (platinichloride, m. p. 236°; aurichloride, m. p. 193°; compare Berlin, A., 1911, i, 426).

Diethylamine reacts less readily with γ-bromopropyl benzoate. *γ-Diethylaminopropyl benzoate* has b. p. 180—181°/22 mm.; *diethyl-γ-hydroxypropylamine*, $OH\cdot C_3H_6\cdot NEt_2$, has b. p. 84°/20 mm., and forms a hygroscopic *methiodide*, m. p. 175°.

When dimethylamine was heated with δ-bromobutyl benzoate, the yield of δ-dimethylaminobutyl benzoate amounted to only 20%, the main product being the quaternary pyrrolidinium benzoate, $C_4H_8NMe_2\cdot OBz$, which is insoluble in acids or ether. Neither could the ester be distilled, for it underwent rearrangement into the same benzoate. This was converted into the *platinichloride*, $C_{12}H_{28}N_2Cl_6Pt$, leaflets, decomp. 226—228°, which was synthesised for comparison from 1-methylpyrrolidine.

Piperidine and γ-bromobutyl benzoate, however, give a high

yield of γ-*piperidinobutyl benzoate*, $C_5H_{10}N \cdot C_4H_8 \cdot OBz$, but this is changed on distillation into the "piperidylpyrrolidinium" benzoate, $CH_2<\begin{matrix}CH_2 \cdot CH_2\\ CH_2 \cdot CH_2\end{matrix}>N(OBz)<\begin{matrix}CH_2 \cdot CH_2\\ CH_2 \cdot CH_2\end{matrix}$. The ester was hydrolysed to 1-δ-*hydroxybutylpiperidine*, $OH \cdot C_4H_8 \cdot NC_5H_{10}$, a viscous liquid, b. p. 129°/18 mm., which forms a *hydrochloride*, leaflets, m. p. 160—161°; a *picrate*, m. p. 109°; and a *methiodide*, m. p. 107°. Two bicyclic quaternary salts (nitrogen spirans) were synthesised for comparison with the above benzoate. By heating together piperidine with dibromo- or di-iodo-butane, or pyrrolidine with dibromopentane, in the presence of 3% sodium hydroxide, the "*piperidylpyrrolidinium*" salts were obtained; *bromide*, m. p. 230°; *iodide*, needles, m. p. 178—180°; *platinichloride*, m. p. 228°; *aurichloride*, m. p. 255°. The latter double salts were also prepared from the above benzoate. Similarly, pyrrolidine and dibromo- or di-iodobutane yielded the "*dipyrrolidinium*" salts, $(C_4H_8)_2⁝N \cdot X$; *platinichloride*, leaflets, m. p. 230°.

ε-Bromoamyl benzoate and diethylamine yield ε-*diethylaminoamyl benzoate*, b. p. 201—202°/20 mm., and this gives *diethyl*-ε-*hydroxyamylamine* as a colourless, almost odourless, viscous liquid, b. p. 125°/18 mm. Similarly, piperidine gives rise to ε-*piperidinoamyl benzoate*, b. p. 226—228°/18 mm., and 1-ε-*hydroxyamylpiperidine*, b. p. 150—152°/22 mm. (*picrate* and *methiodide*, m. p. 65—70°). More tendency to form a quaternary benzoate is exhibited in the pyrrolidine series. ε-Pyrrolidinoamyl benzoate changes on heating into the above "piperidylpyrrolidinium" benzoate, but the crude ester is hydrolysed successfully to 1-ε-*hydroxyamylpyrrolidine*, b. p. 142—143°/19 mm. (*hydrochloride*, m. p. 77—79°; *picrate*, m. p. 84°). Dimethylamine and bromoamyl benzoate give a 60% yield of ε-dimethylaminoamyl benzoate, but this changes on heating into dimethylpiperidinium benzoate, which is characterised as the *platinichloride*,

$$(C_5H_{10}⁚NMe_2)_2PtCl_6,$$

needles, m. p. 210°. The crude ester, however, is converted into *dimethyl*-ε-*hydroxyamylamine*, $OH \cdot C_5H_{10} \cdot NMe_2$, b. p. 115—116°/25 mm., and this yields, in turn, a *methiodide*, leaflets, m. p. 134°, and a *methochloride* ("*pentahomocholine chloride*"), $OH \cdot [CH_2]_5 \cdot NMe_3Cl$, a white, crystalline mass which forms a *platinichloride*, pale yellow needles, m. p. 213°, and an *aurichloride*, brownish-yellow leaflets, m. p. 147°.

The trimethyl-γ-hydroxypropylammonium base (γ-homocholine) is much more physiologically active than choline, but the lengthening of the chain to the above ε-hydroxyamyl compound is not accompanied by any considerable enhancement in this respect.

J. C. W.

Preparation of Halogen Derivatives of Glycineamide. AKTIEN-GESELLSCHAFT FUR ANILINFABRICATION (D.R.-P., 292545; from *J. Soc. Chem. Ind.*, 1916, **35**, 868).—Compounds of the type $NRR'R''X \cdot CH_2 \cdot CO \cdot NH_2$, where R, R′, and R″ are alkyl groups and X a halogen atom, are obtained by the action of ammonia

on alkyl halogentrialkylaminoacetates or of alkyl haloids on dialkylaminoacetamide. They are easily soluble in water and are less toxic than most organic ammonium compounds. G. F. M.

Synthesis of the New Tripeptide, Glycocyamylglycylglycine. A. CLEMENTI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 806—808. Compare A., 1915, i, 77; this vol., i, 91).—*Guanidoglycylglycylglycine* or *glycocyamylglycylglycine*,

$$NH{:}C(NH_2)\cdot[NH\cdot CH_2\cdot CO]_3\cdot OH,$$

prepared by the interaction of diglycylglycine with cyanamide in presence of ammonia, crystallises in needles, is very slightly soluble in water, and towards formol titration behaves as a neutral compound. T. H. P.

Interaction of Iodine and Thioacetamide in Aqueous and Alcoholic Solutions. PRAFULLA CHANDRA RÂY and MANIK LAL DEY (T., 1916, **109**, 698—701).—In the interaction of certain organic thio-compounds with such substances as mercuric, cupric, and platinic chlorides, tautomeric change is known to occur, and in the case of thiocarbamide iodine has also been shown to effect a tautomeric change (Werner, T., 1914, **105**, 2159). Investigation now indicates that iodine exerts a similar effect with thioacetamide in both aqueous and alcoholic solution, this conclusion being drawn from the nature of the products, viz., acetic acid, hydrogen iodide, ammonium iodide, and sulphur in the case of aqueous solutions, and ethyl acetate, ethyl iodide, ammonium iodide, and sulphur in the case of alcoholic solutions. These results are attributed to the primary change $CMeS\cdot NH_2 \longrightarrow SH\cdot CMe{:}NH$, followed by disruption of the latter molecule under the influence of iodine and of the solvent; suggestions are made as to the probable mechanism of the later stages of the changes. D. F. T.

Derivatives of β- and γ-Mercaptopropylamine [Aminopropyl and *iso*Propyl Mercaptans]. WERNER MYLIUS (*Ber.*, 1916, **49**, 1091—1101).—Gabriel and Colman (A., 1912, i, 529) found that β-phthalimidoethylthiol could be transformed into the anhydride of ethylmercaptophthalamic acid, thus:

$$C_6H_4{<}^{CO}_{CO}{>}N\cdot C_2H_4\cdot SH \longrightarrow C_6H_4{<}\begin{matrix}CO\cdot NH\cdot CH_2\\ CO\text{--}S\text{--}CH_2\end{matrix}.$$

The author has now found that the corresponding propyl compounds undergo the same isomerisation.

Potassium phthalimide was condensed with trimethylene chlorobromide, and the resultant γ-chloropropylphthalimide was then boiled with an alcoholic solution of potassium xanthate. The crude ester, $C_8H_4O_2{:}N\cdot C_3H_6\cdot S\cdot CS\cdot OEt$, was finally hydrolysed by means of fuming hydrobromic acid, when a *by-product*, $C_{22}H_{20}O_3N_2S_2$, separated in long, triangular prisms, m. p. 156—157°, leaving the hydrobromide of the desired base in solution. γ-*Mercaptopropylphthalamic anhydride*,

$$C_6H_4{<}\begin{matrix}CO\cdot NH\cdot CH_2\\ CO\text{—}S\text{--}CH_2\end{matrix}{>}CH_2,$$

itself cannot be obtained pure, for it is easily decomposed by water into γ-phthalimidopropyl thiol and the above compound, m. p. 156—157°, which is apparently a further anhydride, 2Base $-$ H_2O. The *hydrobromide* crystallises in four- and six-sided tablets, m. p. 216—217°; the *hydrochloride* forms four-sided prisms, m. p. 203—204°; the *platinichloride* consists of elongated, orange-red tablets, m. p. 192—193°; the *picrate* forms long, yellow needles, m. p. 159—160°; and the *potassium* salt and *nitroso*-compound, yellow prisms, m. p. 121—122° (decomp.), were also prepared. Unlike the salts of the corresponding ethyl compounds, these are soon decomposed by water to γ-phthalimidopropyl thiol.

The corresponding β-propyl compounds cannot be obtained readily from the xanthate, but the analogous ester with ·CO· instead of ·CS· gives good results. β-Bromopropylamine condenses with carbon disulphide to form mercaptomethylthiazoline; this is hydrolysed by boiling with hydrochloric acid to α-aminopropyl-β-thiol, and the base is then converted into the phthalimide. This is condensed with ethyl chloroformate in the presence of sodium methoxide, and the *β-ethylcarbonatothiolpropyl-α-phthalimide*, $C_8H_4O_2$:N·CH_2·CHMe·S·CO_2Et, is isolated in the form of irregular plates, m. p. 111·5—112·5°. On boiling the ester with hydrobromic acid and adding sodium acetate to the solution of the residue left on evaporation, *β-mercaptopropylphthalamic anhydride*, $C_6H_4<\begin{matrix}CO\cdot NH\cdot CH_2\\ CO-S-CHMe\end{matrix}$, is obtained in long prisms or quadratic tablets, m. p. 131°. The base reacts acid to litmus, and is gradually decomposed by boiling water into α-phthalimidopropyl-β-thiol. The following derivatives were prepared: *hydrobromide*, m. p. 219—220°; *hydrochloride*, feathery tufts, m. p. 198°; *platinichloride*, orange-red, rhombic plates, m. p. 211°; *picrate*, m. p. 167°; *nitroso*-compound, rectangular tablets, m. p. 145—146°; *potassium* salt. The *N*-methyl *derivative*, obtained by the action of methyl iodide, is easily decomposed by water, but the *hydriodide*, long prisms, m. p. 201—202°, and the *picrate*, glistening plates, m. p. 160—161°, can be prepared.

The above α-phthalimidopropyl-β-thiol was also methylated, and the *methyl α-phthalimido*iso*propyl sulphide*,

$C_8H_4O_2$:N·CH_2·CHMe·S·CH_3,

m. p. 57—58°, was hydrolysed to *methyl α-amino*iso*propyl sulphide*, SMe·CHMe·CH_2·NH_2, a strongly alkaline, mobile liquid, b. p. 158°/763 mm. The following derivatives of the base were prepared: *picrate*, m. p. 133—134°; *methiodide*,

SMe·CHMe·CH_2·NMe_3I,

m. p. 162—163°; *thiocarbimide*, SMe·CHMe·CH_2·N:CS, a mustard-oil which condensed with aniline to form the *compound*,

NHPh·CS·NH·CH_2·CHMe·SMe,

m. p. 48—53°; *sulphone*, SO_2Me·CHMe·CH_2·NH_2, b. p. 140°/4 mm. (*hydrochloride*, m. p. 111—112°; *picrate*, m. p. 160—161°; *oxalate*, m. p. 181—182°).

The corresponding *ethyl aminoisopropyl sulphide*,

$$SEt\cdot CHMe\cdot CH_2\cdot NH_2,$$

has b. p. 170—171°/756 mm., and forms a *picrate*, m. p. 131—132°. J. C. W.

Alloxantin. TORSTEN THUNBERG (*Skand. Arch. Physiol.*, 1916, **33**, 217—222).—Experiments on the autoxidation of dialuric acid lead to the conclusion that alloxantin is the alloxan salt of dialuric acid, a relationship expressed by Richter's oxonium formula for alloxantin (A., 1911, i, 757). The author considers that his results have a bearing on the constitution of quinhydrones. G. B.

Thiocyanates and Thiocarbimides. IX. Ethyl Thiocarbiminoacetate. TREAT B. JOHNSON and E. HEATON HEMINGWAY (*J. Amer. Chem. Soc.*, 1916, **38**, 1550—1557).—Ethyl thiocarbiminoacetate, $SCN\cdot CH_2\cdot CO_2Et$, is prepared by the action of thiocarbonyl chloride (rather more than 1 mol.) on ethyl aminoacetate hydrochloride suspended in boiling toluene. The substance, which was first prepared by Klason in 1890, is a colourless oil, becoming red by keeping, b. p. 215° (decomp.) or 112—113°/12 mm., D^{20} 1·1710, n_D^{20} 1·5028 (Pulfrich) and 1·5038 (Abbe). It reacts with dry ammonia in benzene to form 2-thiohydantoin and with aromatic primary amines in boiling ether to form *ethyl arylthiohydantoates*, $NHAr\cdot CS\cdot NH\cdot CH_2\cdot CO_2Et$; Ar = p-*tolyl*, needles, m. p. 96°; Ar = o-*tolyl*, m. p. 90°; Ar = m-*tolyl*, prismatic needles, m. p. 97°; Ar = *p*-nitrophenyl, rosettes of yellow needles, m. p. 191·5°.

Thiocarbonyl chloride does not react with glycine hydrochloride in boiling toluene. C. S.

Direct Nitration of Aliphatic Imino-compounds. I. Action of Absolute Nitric Acid on 3 : 5-Diketo-1-methylhexahydro-1 : 4-diazine. J. V. DUBSKY [with J. PETTERS] (*Ber.*, 1916, **49**, 1037—1040).—Franchimont and Dubsky have shown that when certain derivatives of iminodiacetic acid are treated with pure nitric acid, the hydrogen atom of the imino-group is replaced by the nitro-group (A., 1912, i, 752). Methyliminodiacetimide (3:5-diketo-1-methylpiperazine), however, behaves differently, the two methylene groups being oxidised to ketone groups.

Methyl methyliminodiacetate, $NMe(CH_2\cdot CO_2Me)_2$, b. p. 114·5—115·5°/13 mm., was prepared by the action of methyl sulphate on methyl iminodiacetate, and converted through the diamide into the imide (*ibid.*). This was boiled with pure nitric acid for a few minutes, and then the solution was left in a vacuum, when 2:3:5:6-*tetraketo*-1-*methylpiperazine*, decomp. 280°, crystallised out. J. C. W.

Imino-di-*iso*butyronitrile. J. V. DUBSKY and [FRL.] W. D. WENSINK (*Ber.*, 1916, **49**, 1134—1140).—The preparation and hydrolysis of iminodi*iso*butyronitrile for the purposes of the investigation of the action of pure nitric acid (compare preceding abstract) were found to be exceptionally difficult. Small quantities of α-amino-*iso*butyronitrile (Snesarev, A., 1914, i, 671) could readily be con-

verted into the nitrile on watch-glasses, but the scale of the operation could not be enlarged. Hydrolysis by means of concentrated hydrochloric acid or barium hydroxide merely gave acetone, hydrogen cyanide, and α-amino*iso*butyric acid, whilst 20% or concentrated sulphuric acid gave an anhydride of this acid, 2 : 2 : 5 : 5-tetramethylpiperazine. The hydrogen peroxide method only gave a small yield of a compound of uncertain composition. Moreover, the nitrile differed from iminodi-aceto- and -propio-nitriles in being uninfluenced by pure nitric acid.

Two convenient methods for the preparation of **α-amino*iso*-butyronitrile** from acetone are described, and also the best conditions for obtaining the α-iminodi*iso*butyronitrile, $NH(CMe_2{\cdot}CN)_2$ (*ibid.*). 2 : 2 : 5 : 5-*Tetramethylpiperazine* crystallises in glistening needles, which sublime at 210°. *α-Amino*iso*butyric acid* forms a hygroscopic *hydrochloride* and a deep violet *copper* salt. The *compound*, m. p. 155—162°, obtained by hydrolysing the nitrile with alkaline hydrogen peroxide, was apparently the expected diamide condensed with acetone, one of the chief products of hydrolysis, thus: $CMe_2[N(CMe_2{\cdot}CO{\cdot}NH_2)_2]_2$. J. C. W.

Direct Nitration of Aliphatic Imino-compounds. III. Action of Absolute Nitric Acid on Derivatives of Iminodipropionic Acid. J. V. DUBSKY [with (FRAU) ST. IZDEBSKA-DOMANSKA and (FRL.) W. D. WENSINK] (*Ber.*, 1916, **49**, 1045—1060).—The preparation of αα′-iminodipropionitrile, $NH(CHMe{\cdot}CN)_2$, by one or two methods is described, the most expeditious being as follows: a well-cooled suspension of ammonium chloride in an ethereal solution of acetaldehyde is shaken with potassium cyanide solution, left overnight, and then treated successively with acetic acid, acetaldehyde, and potassium cyanide, when the ethereal layer is finally evaporated. The nitrile, m. p. 68°, forms a *nitrate* with dilute nitric acid, in white crystals, m. p. 100—103° (decomp.), and reacts with pure nitric acid to form *nitro-αα′-iminodipropionitrile*, $NO_2{\cdot}N(CHMe{\cdot}CN)_2$, in snow-white leaflets, m. p. 96° (the first preparation was yellow and had m. p. 103°). All the specimens of the nitrile examined yielded the more fusible of the two αα′-iminodipropionic acids, m. p. 235°, on hydrolysis (compare Ciamician and Silber, A., 1907, i, 19). This was purified by means of the *zinc* salt, $NH(CHMe{\cdot}CO_2)_2Zn$, which forms very sparingly soluble, microscopic, quadratic tablets. Other salts described are: *ammonium hydrogen* salt, small, glistening tablets, m. p. 230—235°; *copper* salt, a bluish-green powder; *barium* salt, alkaline to litmus; *barium hydrogen* salt, faintly alkaline. The acid also forms a *nitrate*, decomp. 140°, and reacts with pure nitric acid to yield *nitroiminodipropionic acid*, $NO_2{\cdot}N(CHMe{\cdot}CO_2H)_2$, which crystallises in stout needles, decomp. 175—180°, and gives *ammonium, sodium, copper, zinc, barium*, and *calcium* salts.

Dimethyl iminodipropionate, b. p. 122—124°/30 mm., was converted into the *diamide*, $NH(CHMe{\cdot}CO{\cdot}NH_2)_2$, m. p. 127°, and this was hydrolysed to the monoamide (amic acid) (*ibid.*) by the

hydrogen peroxide method. The latter gave a small yield of the imide, 3:5-diketo-2:6-dimethylpiperazine (*ibid.*) on sublimation, whilst the diamide, when heated for some hours at 120—130°, gave this and a small amount of a *compound*, m. p. 207°, probably of the formula $NH:(CHMe\cdot CO)_2:N\cdot NH_4$, which is insoluble in ethyl acetate. The imide reacts with pure nitric acid to form 1-*nitro*-3:5-*diketo*-2:6-*dimethylpiperazine*,

$$NO_2\cdot N:(CHMe\cdot CO)_2:NH,$$

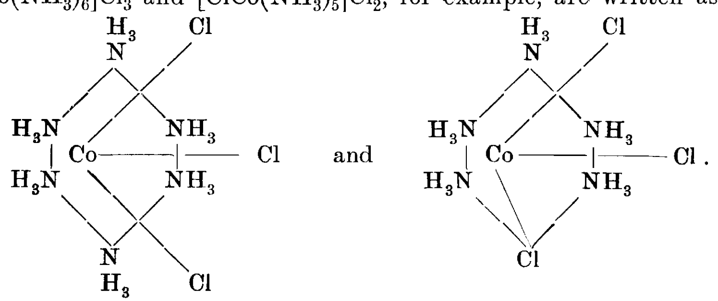
decomp. 136—138°, and with acetic anhydride to form the 1-*acetyl* compound, m. p. 174°. J. C. W.

Action of Mercuric Cyanide on Salts and Ester-salts of Thiosulphuric Acid. A. GUTMANN (*Ber.*, 1916, **49**, 949—954).—According to Kessler (1849), the action of mercuric cyanide on sodium thiosulphate or the polythionates results in the formation of sodium sulphate, hydrogen cyanide, mercuric sulphide, and sulphur, but not of thiocyanates, which is opposed to the behaviour of potassium cyanide as determined by the author (A., 1906, i, 149). It is now found that the result depends on the reaction of the solution.

In neutral solutions, mercuric cyanide and barium thiosulphate react according to the equation: $Hg(CN)_2 + 2BaS_2O_3 + H_2O = HgS + BaSO_3 + BaSO_4 + HCN + HCNS$, whilst the reaction in alkaline solutions is represented by $4Hg(CN)_2 + 8Na_2S_2O_3 + Na_2O = 3Hg(CNS)_2 + NaCNS + NaCN + HgS + 7Na_2SO_3 + Na_2SO_4$, from which it appears probable that thiosulphuric acid exists in two tautomeric forms (compare A., 1907, i, 671). Kessler's reaction takes place in acid solutions: $Hg(CN)_2 + BaS_2O_3 + H_2O = HgS + 2HCN + BaSO_4$ and $BaS_2O_3 + 2HCl = BaCl_2 + SO_2 + S + H_2O$.

Mixtures of solutions of mercuric cyanide and sodium ethyl (or benzyl) thiosulphate soon become acid, and the reaction therefore follows the latter course, thus: $2NaSO_2\cdot OSEt + Hg(CN)_2 + 2H_2O = 2NaHSO_4 + 2HCN + Hg(SEt)_2$. J. C. W.

A Cyclic Theory of the Constitution of Metalammines and of Ferro- and Ferri-cyanides. JOHN ALBERT NEWTON FRIEND (T., 1916, **109**, 715—722).—After stating various objections to Werner's method of formulating the complex cobaltammines, the author puts forward a cyclic constitution for these and other compounds (compare Friend, T., 1908, **90**, 1006). The formulæ for $[Co(NH_3)_6]Cl_3$ and $[ClCo(NH_3)_5]Cl_2$, for example, are written as:



According to this method of formation: (1) The dissociable chlorine atoms are attached directly to the cobalt atom. (2) The cobalt and chlorine atoms are credited with valency values that are strictly in accord with their known behaviour. (3) In the pentammine salt the one chlorine atom is incapable of separate dissociation, not because it is attached to the cobalt, but because it forms part of the ring. (4) The cobalt atom lies in the ring, from which it cannot escape for purely physical reasons.

It follows that $[Cl_2Co(NH_3)_4]Cl$, which will contain two chlorine atoms in the ring, should give three isomerides, whereas only two are known. In the case of $[Cl_3Co(NH_3)_3]$, all the chlorine atoms are in the ring, so that ionisation cannot take place, which is in accordance with the facts; however, three different isomerides should exist, whereas only one compound is known.

A cyclic constitution is also given to the ferro- and ferri-cyanides and to Prussian-blue, the iron atom being situated within a ring composed of carbon and nitrogen atoms; both the iron and potassium atoms are united to nitrogen, the iron, as in the case of cobalt in the cobaltammines, being unable to ionise because it is within the ring. The formulæ explain the existence of isomeric potassium ferro- and ferri-cyanides, and also some of the known facts in connexion with Prussian-blue. T. S. P.

The Rare Earth Cobalticyanides. C. JAMES and P. S. WILLAND (*J. Amer. Chem. Soc.*, 1916, **38**, 1497—1500. Compare this vol., ii, 102).—Further investigation has shown that the rare earth cobalticyanides separate out in the form of crystals which can be represented by the general formula $R_2(CoC_6N_6)_2,9H_2O$. A comparison of the solubilities of the cobalticyanides in 10% hydrochloric acid (D^{15} 1·050) gave the following results, expressing the number of parts of each salt contained in 1000 parts of saturated solution: lanthanum, 10·41; cerium, 10·75; neodymium, 4·19; gadolinium, 1·86; ytterbium, 0·38; yttrium, 2·78.

Fractional crystallisation experiments show that a rapid separation may be attained by the cobalticyanide method, and the method is particularly recommended for the separation of yttrium from erbium. H. M. D.

Preparation of Guanidine Sulphate. P. A. LEVENE and JAMES K. SENIOR (*J. Biol. Chem.*, 1916, **25**, 623—624).—The starting material is dicyanodiamide, which is prepared from crude commercial calcium cyanamide by the method of Söll and Stutzer (A., 1910, i, 14). About 100 grams of dicyanodiamide are mixed in a 2-litre wide-mouthed, round-bottomed flask with 200 c.c. of 75% sulphuric acid. After about two minutes the mixture becomes very hot, and a violent evolution of carbon dioxide occurs. When this spontaneous reaction has nearly ceased, the flask is gently heated for five minutes at a temperature sufficient to keep a good stream of gas coming off, and is then allowed to cool. At the moment when the contents begin to solidify, 1500 c.c. of 95% alcohol are added, and the mixture is cooled in the ice-chest overnight. The

ammonium sulphate which separates is filtered off and washed with 95% alcohol. The filtrate and washings are concentrated to about 300 c.c., and neutralised whilst hot with barium carbonate. After removal of the precipitated barium salts, the liquid is concentrated to a viscous oil, which is then poured into a litre of 95% alcohol. On stirring and scratching, the oil solidifies into a crystalline mass, which is collected and dried at 100°. The yield is about 125 grams. H. W. B.

Preparation of Sulpho-chlorides of the Naphthalene Series. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 292357; from *J. Soc. Chem. Ind.*, 1916, **35**, 830).—Acyl-β-naphthylamines on treatment with chlorosulphonic acid are converted into sulpho-chlorides. Acyl-α-naphthylamines, treated similarly, yield sulphonic acids. G. F. M.

Triphenylmethyl. XXVI. Tautomerism of Triarylcarbinols. M. GOMBERG and N. E. VAN STONE (*J. Amer. Chem. Soc.*, 1916, **38**, 1577—1606).—The paper opens with an account of the historical development of the application of the tautomeric hypothesis to the triphenylmethane derivatives, leading up to the discovery of the two desmotropic forms of *p*-hydroxytriphenylcarbinol (Gomberg, A., 1913, i, 1056). The final period in the development has not yet been attained; two desmotropic chlorides or sulphates in the solid, crystalline state have not yet been prepared. As a near approach to the realisation of this may be considered the fact that, whilst the triarylcarbinyl chlorides are colourless, another set of analogous acid derivatives, the sulphates, are always coloured. A still nearer approach to this realisation are some of the results described in connexion with arylxanthenols (Gomberg and West, A., 1913, i, 72).

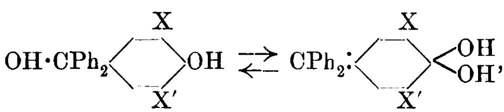
The object of the present investigation is to extend the discovery of a single carbinol existing in two desmotropic forms to various substituted triphenylcarbinols, having in view the effects on the tautomeric tendency which may be brought about by various groups in the benzene ring. For the present have been studied only carbinols containing substituents in the *p*-hydroxyphenyl group.

The condensation of diphenylmethylene dichloride with a phenol (Gomberg and Jickling, this vol., i, 29) offers a very general method for the synthesis of *p*-hydroxytriphenylcarbinols. *o*-Cresol, guaiacol, and *o*-bromo-, *o*-chloro, and *o*-nitro-phenols have been employed, and except in the case of the nitrophenol, a reaction analogous to the first step recorded by Gomberg and Jickling takes place without the aid of a catalyst; the various diphenoxydiphenylmethanes have been isolated. With guaiacol and *o*-cresol the reaction proceeds easily through the second step to the formation of the substituted *p*-hydroxytriphenylcarbinols, but with the chloro- and bromo-phenols the reaction stops at the first step. The best method to obtain the desired carbinols is the reaction between *o*-chloro- or *o*-bromo-phenol and diphenylmethylene dichloride in carbon disul-

phide in the presence of anhydrous aluminium chloride. By long keeping or by reacting at an elevated temperature diphenylmethylene dichloride and *o*-cresol or guaiacol yield the tetraphenyl derivative. From *o*-nitrophenol, the desired nitrohydroxytriphenylcarbinol could not be obtained even by warming, by the addition of a drop of sulphuric acid, or by the use of aluminium chloride and carbon disulphide; only when the two substances are treated with aluminium chloride without a solvent was the desired compound obtained.

By brominating and chlorinating the carbinols obtained from *o*-cresol, guaiacol, and *o*-chloro- and *o*-bromo-phenols, carbinols substituted in both ortho-positions with respect to the para-hydroxyl group were obtained.

In the case of every carbinol except that obtained from *o*-nitrophenol two distinct forms were obtained, the colourless benzenoid (I) and the coloured quinonoid (II):



(I.) (II.)

where X = Me, OMe, Br, or Cl, and X′ = H, Br, or Cl.

The colourless form is best obtained by dissolving the carbinol in *N*-alkali, precipitating with carbon dioxide, and crystallising from benzene, ether, or alcohol. The quinonoid form is always obtained by crystallising the benzenoid form from 60% to 70% acetic acid, heat being necessary in some cases to effect a complete change. If more dilute acid is used (30—40%) a mixture of the two forms is obtained; if more concentrated acid is employed, the fuchsone or a carbinyl acetate is liable to be obtained. The change from the colourless to the coloured form is effected by heat, and slowly by light, in the absence of a solvent.

The following are the compounds obtained: *Di*-o-*tolyloxydiphenylmethane*, $CPh_2(O{\cdot}C_6H_4Me)_2$, colourless crystals, m. p. 142°; 4-hydroxy-3-methyltriphenylcarbinol [diphenyl-6-hydroxy-*m*-tolylcarbinol], benzenoid form, colourless crystals, m. p. 148—149°; quinonoid form, intense yellow crystals, m. p. 108—109° (compare Bistrzycki and Zurbriggen; Bistrzycki and Herbst, A., 1904, i, 44); ωω-diphenyl-2-methylquinomethane, deep red crystals, m. p. 176° (compare Bistrzycki and Zurbriggen, *loc. cit.*), and its *acetate*, $C_{20}H_{16}O,C_2H_4O_2$, deep red crystals, which lose acetic acid at 75°; *diphenyl*-6 : 6′-*dihydroxydi*-m-*tolylmethane*, $CPh_2(C_6H_3Me{\cdot}OH)_2$, colourless crystals, m. p. 190°.

Diphenyl-5-*bromo*-6-*hydroxy*-m-*tolylcarbinol*, $C_{20}H_{17}O_2Br$, benzenoid form, colourless crystals, m. p. 145°, quinonoid form, red crystals, m. p. 138—139°; *perbromide*, deep red crystals; 6-*bromo*-ωω-*diphenyl*-2-*methylquinomethane*, $CPh_2{:}C_6H_2MeBr{:}O$, orange-red crystals, m. p. 202°.

Diphenyl-5-*chloro*-6-*hydroxy*-m-*tolylcarbinol*, $C_{20}H_{17}O_2Cl$, quin-

onoid form, yellow crystals, m. p. 133°; benzenoid form, colourless crystals, m. p. 149°; *6-chloro-ωω-diphenyl-2-methylquinomethane*, $CPh_2{:}C_6H_2MeCl{:}O$, orange crystals, m. p. 197°, which is far more stable to heat than the other analogues examined.

2 : 2′-*Dimethoxydiphenoxydiphenylmethane*, $CPh_2(O{\cdot}C_6H_4{\cdot}OMe)_2$, colourless crystals, m. p. 189°; *4-hydroxy-3-methoxytriphenylcarbinol*, $C_{20}H_{18}O_3$, benzenoid form, colourless crystals, m. p. 159°; quinonoid form, brown crystals, m. p. 147°; *2-methoxy-ωω-diphenylquinomethane*, $CPh_2{:}C_6H_3(OMe){:}O$, m. p. 183°, which is less stable towards heat than any other fuchsone examined, the methoxybenzoquinone resulting from the decomposition has m. p. 145° (compare Moore, T., 1911, **99**, 1045), not 140°, as stated in the literature; 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxytetraphenylmethane*,

$$CPh_2[C_6H_3(OH)(OMe)]_2,$$

m. p. 208°, softening at 200°.

5-*Bromo-4-hydroxy-3-methoxytriphenylcarbinol*, $C_{20}H_{17}O_3Br$, benzenoid form, colourless crystals, m. p. 156°; quinonoid form, orange crystals, m. p. 151°; *6-bromo-2-methoxy-ωω-diphenylquinomethane*, $CPh_2{:}C_6H_2Br(OMe){:}O$, dark red crystals, m. p. 232°.

5-*Chloro-4-hydroxy-3-methoxytriphenylcarbinol*, $C_{20}H_{17}O_3Cl$, quinonoid form, orange crystals, m. p. 159—161°; benzenoid form, colourless crystals, m. p. 166—168°; *6-chloro-2-methoxy-ωω-diphenylquinomethane*, m. p. 227°.

2 : 2′-*Dibromodiphenoxydiphenylmethane*, $CPh_2(O{\cdot}C_6H_4Br)_2$, crystals, m. p. 184—185°; *3-bromo-4-hydroxytriphenylcarbinol*, $C_{19}H_{15}O_2Br$, benzenoid form, colourless crystals, m. p. 109°; quinonoid form, orange crystals, m. p. 104·5—105°; *2-bromo-ωω-diphenylquinomethane*, $CPh_2{:}C_6H_3Br{:}O$, m. p. 140°.

3 : 5-*Dibromo-4-hydroxytriphenylcarbinol*, $C_{19}H_{14}O_2Br_2$, benzenoid form, m. p. 138°; quinonoid form, red crystals, m. p. 134—136°; the *dibromofuchsone* forms orange-red crystals.

2 : 2′-*Dichlorodiphenoxydiphenylmethane*, $CPh_2(O{\cdot}C_6H_4Cl)_2$, m. p. 191—192°; *3-chloro-4-hydroxytriphenylcarbinol*, $C_{19}H_{15}O_2Cl$, benzenoid form, white powder, m. p. 126°; quinonoid form, orange crystals, m. p. 118°; *2-chloro-ωω-diphenylquinomethane*, m. p. 162—163° (*acetate*, deep red crystals, which lose acetic acid at 75°).

3 : 5-*Dichloro-4-hydroxytriphenylcarbinol*, $C_{19}H_{14}O_2Cl_2$, benzenoid form, m. p. about 134°; quinonoid form, red crystals, m. p. about 134°; the *dichlorofuchsone* has m. p. 217°.

3-*Nitro-4-hydroxytriphenylcarbinol*, $C_{19}H_{15}O_4N$, has been obtained only in one form, almost colourless crystals, m. p. 97—98°; its *sodium* salt is bright red, whereas those of the preceding carbinols are all colourless.

The benzenoid structure ascribed to the colourless forms of the preceding carbinols requires no further explanation, it being in harmony with the generally accepted view as regards this class of compounds. The authors' justification for ascribing the quinonoid structure to the coloured forms rests on the analogy to the triaryl haloids in the coloured form, the relation to the fuchsone, and particularly on the rate of dehydration under the influence of heat

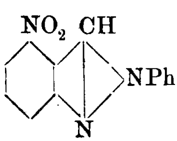
as compared with that of the benzenoid form. The two forms of a carbinol are heated at a temperature (75°) at which the change from the benzenoid to the quinonoid form is slow as compared with the loss of water from the coloured compound, and the loss of water with time is noted; in all cases the loss of water by the coloured form is very much greater than that by the colourless form, the latter losing water slowly in proportion as it is being transformed into the quinonoid desmotrope under the influence of heat energy. The dehydration curves show that the benzenoid forms of the various carbinols differ, according to the nature of the substituent X (see above), in their readiness to transform into the coloured desmotropes.

An attempt has been made to isolate the free radicle in the case of diphenyl-6-hydroxy-*m*-tolylcarbinol. The carbinol was converted by *N*-alkali and ethyl chlorocarbonate at 0° into *diphenyl-6-ethylcarbonato-*m*-tolylcarbinol*, $OH\cdot CPh_2\cdot C_6H_3Me\cdot O\cdot CO_2Et$, crystals, m. p. 136°, which was converted by the usual method for the preparation of triaryl chlorides into *diphenyl-6-ethylcarbonato-*m*-tolylcarbinyl chloride*, $C_{23}H_{21}O_3Cl$, colourless rosettes, m. p. 131—132°. The latter in benzene solution, by treatment with molecular silver, forms a lemon-yellow solution which rapidly absorbs oxygen, forming a *peroxide*, m. p. about 161—162°. There can be no doubt, therefore, that the free radicle actually exists, but all attempts to isolate it failed. C. S.

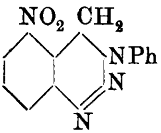
Preparation of 2 : 9 : 10-Trichloroanthracene. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 292356; from *J. Soc. Chem. Ind.*, 1916, **35**, 830).—Anthracene or 9 : 10-dichloroanthracene is heated in a steam-bath with sulphuryl chloride in presence of an indifferent solvent or diluent such as nitrobenzene. On cooling, 2 : 9 : 10-trichloroanthracene separates, and is purified by crystallisation from benzene. G. F. M.

Some Derivatives of 2 : 6-Dinitrobenzylaniline. S. REICH and M. GHAZARIAN (*Bull. Soc. chim.*, 1916, [iv], **19**, 259—264).—*o*-Nitrobenzylaniline when reduced with tin and hydrochloric acid does not give aminobenzylaniline, but phenylindazole (compare Paal, A., 1891, 723), and the authors now find that 2 : 6-dinitrobenzylaniline, when reduced in this way, is converted even more readily into an indazole derivative.

When a freshly prepared solution of stannous chloride in hydrochloric acid is added to an alcoholic solution of 2 : 6-dinitrobenzylaniline, *4-nitrophenylindazole*, yellowish-green crystals, m. p. 156—157° (annexed formula), is immediately precipitated in theoretical quantity in the form of its *stannichloride*.



If the reduction is brought about by alcoholic ammonium sulphide, it proceeds normally, and the product is *6-nitro-2-aminobenzylaniline*, yellow needles, m. p. 143—144°, giving a *benzylidene* derivative, red crystals, m. p. 157°. When this base is dissolved in dilute



hydrochloric acid and to the solution cooled to 0° the calculated quantity of sodium nitrite is gradually added, the product is 5-*nitro*-3-*phenyl*-3 : 4-*dihydro*-1 : 2 : 3-*benztriazine*, brownish-yellow crystals, m. p. 153—154° (decomp.) (annexed formula).

Contrary to the results obtained with *o*-nitrobenzylacetanilide by Paal and Krecke (compare A., 1890, 1443), but in agreement with those obtained with *o*-nitrobenzylbenzanilide by Söderbaum and Widmann (compare A., 1890, 1258), the authors find that when 2 : 6-dinitrobenzylacetanilide and the corresponding benzanilide are reduced they give amines, no ring formation occurring.

2 : 6-*Dinitrobenzylacetanilide*, m. p. 137—138°, obtained by warming the aniline on a water-bath for two hours with excess of acetic anhydride, on reduction with alcoholic ammonium sulphide yields 6-*nitro*-2-*aminobenzylacetanilide*, yellow needles, m. p. 160—161°. This base, when warmed with acetic anhydride, gives 6-*nitro*-2-*acetylaminobenzylacetanilide*, m. p. 147°.

2 : 6-*Dinitrobenzylbenzanilide*, m. p. 145°, is obtained by heating the corresponding aniline with benzoyl chloride in pyridine solution, and on reduction it yields 6-*nitro*-2-*aminobenzylbenzanilide*, m. p. 134—136°. W. G.

Derivatives of 1 : 2 : 3 : 4-Tetrahydro-β-naphthylamine. ERNST WASER (*Ber.*, 1916, **49**, 1202—1207).—Bamberger and Filehne (A., 1889, 737) found that *ac*-tetrahydro-β-naphthylamine and its *N*-dimethyl- and -ethyl derivatives, unlike other tetrahydronaphthylamines, were physiologically active. Other derivatives of the base have now been prepared for pharmacological studies.

Ethyl 1 : 2 : 3 : 4-*tetrahydro*-β-*naphthylcarbamate*,

$$C_6H_4<\begin{matrix}CH_2\cdot CH\cdot NH\cdot CO_2Et\\ CH_2\cdot CH_2\end{matrix},$$

was obtained by mixing ethereal solutions of the base and ethyl chloroformate, in rosettes of needles, m. p. 82°. 1 : 2 : 3 : 4-*Tetrahydro*-β-*naphthylethylthiocarbamide*, $C_{10}H_{11}\cdot NH\cdot CS\cdot NHEt$, formed four-sided prisms, m. p. 131·5°. 1 : 2 : 3 : 4-*Tetrahydro*-β-*naphthyldimethylamine* was prepared by converting the tetrahydronaphthyltrimethylammonium iodide into the chloride and distilling this; it was found to be a colourless, mobile, fluorescent oil, b. p. 132·3—133·3° (corr.)/11 mm., which yielded a *hydrochloride*, silky leaflets, m. p. 214—215° (decomp.), and a *platinichloride*, orange-red needles, m. p. 210° (decomp.). The corresponding *naphthylmethylamine*, $C_{10}H_{11}\cdot NHMe$, was obtained by the action of methyl sulphate in the cold, as a mobile oil, b. p. 118—119·8° (corr.)/9 mm., D_4^{20} 1·024, which yielded a *hydrochloride*, m. p. 214°, and a *platinichloride*, m. p. 228° (decomp.).

1 : 4-Dihydronaphthalene was treated with a solution of hypochlorous acid with the hope of obtaining a chlorohydrin, but the product which remained was 2 : 3-*dichloro*-1 : 2 : 3 : 4-*tetrahydronaphthalene*. This crystallised in long needles, m. p. 84—85°.

J. C. W.

New Products of the Electrochemical Oxidation of Phenol. FR. FICHTER and ÉMILE BRUNNER (*Bull. Soc. chim.*, 1916, [iv], **19**, 281—287).—On submitting phenol in comparatively concentrated solution in dilute sulphuric acid to electrochemical oxidation, the authors have proved the presence in the oxidation products of quinol, benzoquinone, and catechol (compare Fichter and Stocker, A., 1914, i, 946), of 4:4′-diphenol (compare Drechsel, A., 1884, 1136; 1888, 1276), and also of 2:4′-diphenol and *o*-hydroxydiphenyl ether, $OH\cdot C_6H_4\cdot O\cdot C_6H_5$, together with a large amount of resinous substances. The diphenols are in all probability intermediate products in the formation of benzoquinone and the dihydroxybenzenes, since on submitting them to similar oxidation they yield the latter products. W. G.

Mononitrophenyl Ethers. HILTON IRA JONES and ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1916, **38**, 1534—1550).—Potassium phenoxide is best prepared by first fusing phenol (50 grams) and potassium hydroxide (35 grams, purified by alcohol) separately and stirring the molten hydroxide into the phenol, the product being gently heated, with constant stirring, until it just begins to form a hard ball, when it is removed to a flask, which is then tightly corked; the product is best powdered while still hot. The method is applicable to all phenols which do not contain a nitro-group.

o-Nitrodiphenyl ether, prepared by heating potassium phenoxide and *o*-bromonitrobenzene without a solvent on the water-bath and distilling the product in a vacuum, is a golden-yellow liquid, b. p. 195—197° (decomp.)/45 mm. (at 13 mm. boils without decomposition), $D^{21\cdot5}$ 1·2539, n^{20} 1·575. By heating with concentrated sulphuric acid it forms a *sulphonic acid*, $NO_2\cdot C_6H_4\cdot O\cdot C_6H_4\cdot SO_3H$, radial flakelets like hoar-frost, m. p. 90° (decomp.) (prepared from the *cadmium* salt); other salts described are those of *sodium*, *potassium*, *calcium*, *strontium*, *barium*, *copper*, *silver*, and *lead*. The *sulphonyl chloride*, prepared from the sodium salt and phosphorus pentachloride, crystallises in needles. o-*Aminodiphenyl ether hydrochloride*, scales, m. p. 154° (decomp.), prepared by reducing the nitro-compound with stannous chloride, yields the *base*, crystals, decomp. 43—45°, by treatment with ammonia. Its diazotised solution (the *diazonium chloride* forms crystals, which burn but do not explode when heated) has been coupled with a large number of aromatic monoamines and diamines and mono- and poly-hydric phenols. The sulphonated aminodiphenyl ether has also been diazotised and coupled with amines and phenols. The properties of all these dyes, and also those of *p*-aminodiphenyl ether and of its sulphonic acid (see below), have been studied.

p-Nitrodiphenyl ether, prepared in a similar manner to the ortho-compound, forms needles, m. p. 123·5° (previous observers record m. p.'s in the neighbourhood of 60°), b. p. 320° (slight decomp.), and forms a *sulphonic acid*, crystals, m. p. 132°, by heating on the water-bath with 33% fuming sulphuric acid, the acid separating directly on pouring into water.

p-Aminodiphenyl ether hydrochloride is easily obtained by reducing the nitro-compound dissolved in alcohol with tin and hydrochloric acid. The base has m. p. 95°; Haeussermann and Teichmann give 84°, Nollau and Daniels 33—34°.

o-Nitrodiphenyl ether and all its compounds are more soluble than the corresponding para-compounds and do not crystallise so well. *p*-Nitrodiphenyl ether and all its derivatives are more stable than the corresponding ortho-compounds. The ortho-ether is more easily sulphonated and is more difficult to reduce, and its amino-derivative is more easily diazotised than the para-compound.

Dyes of the *o*-amino-series are more brilliant than those of the para-series, and tend mostly to reds and browns; a few purple and yellow dyes have been produced. The sulphonated dyes are less brilliant than the unsulphonated.

A chronological bibliography of the phenyl ethers is appended.

C. S.

Preparation of a Bromo-derivative of *p*-Aminophenyl Salicylate. I. ABELIN and S. LICHTENSTEIN-ROSENBLATT (D.R.-P., 291878; from *J. Soc. Chem. Ind.*, 1916, **35**, 867).—An α-bromo-*iso*valeryl derivative of *p*-aminophenyl salicylate,

$$OH\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot NH\cdot CO\cdot C_4H_8Br,$$

is obtained either by the action of an α-bromo*iso*valeryl haloid on *p*-aminophenyl salicylate or by the bromination of the *iso*-valeryl derivative of *p*-aminophenyl salicylate. The new substance is sedative, soporific, and antirheumatic. It produces a gradual lowering of temperature, acts as an internal disinfectant, and is only slightly toxic. G. F. M.

***m*-Phenetidine and some of its Derivatives.** FRÉDÉRIC REVERDIN and J. LOKIETEK (*Bull. Soc. chim.*, 1916, [iv], **19**, 252—259; *Arch. Sci. phys. nat.*, 1916, [iv], **42**, 47—55. Compare A., 1915, i, 524, 878).—When acetyl-*m*-phenetidide is nitrated, the three principal products are 6-nitroaceto-*m*-phenetidide, 4-nitroaceto-*m*-phenetidide, and 4 : 6-dinitroaceto-*m*-phenetidide in amounts varying according to the conditions of nitration. To prepare the isomeric mononitro-derivatives, the aceto-*m*-phenetidide is best nitrated in acetic acid solution by running in the nitric acid (D 1·4) and keeping the temperature between 0—5°, and finally allowing it to rise to 30°. The product is poured on to ice, the precipitate is dried, and the isomerides separated by means of light petroleum. 4-*Nitroaceto*-m-*phenetidide* is readily soluble, and is finally obtained in almost colourless needles, m. p. 95°. It is readily hydrolysed by warming it with concentrated sulphuric or hydrochloric acid, giving 4-*nitro*-m-*phenetidine*, citron-yellow needles, m. p. 105—106°. The constitution of these two compounds is proved by the ready conversion of the phenetidide into 4-nitroacetyl-*m*-aminophenol, m. p. 262—263° (compare Meldola, T., 1914, **105**, 997). The portion of the nitration product insoluble in light petroleum is recrystallised from water, giving 6-*nitroaceto*-m-*phenetidide*, pale yellow needles, m. p. 147°, which

on hydrolysis gives 6-*nitro*-m-*phenetidine*, white needles, m. p. 122—123°. This base when diazotised and the product decomposed yields the ethyl ether of 4-nitroresorcinol, m. p. 130—131° (compare Weselsky and Benedikt, A., 1881, 726).

4:6-*Dinitroaceto*-m-*phenetidide* is best prepared by nitrating aceto-*m*-phenetidide in sulphuric acid solution with nitric acid (D 1·5) at a temperature of 0°, and submitting the product from this, when poured on to ice, to further nitration by adding it to nitric acid (D 1·5), the temperature of which is not allowed to rise above 10°. The nitro-compound finally obtained crystallises from acetone or benzene in almost colourless needles, m. p. 125°, and when boiled with concentrated hydrochloric acid yields 4:6-*dinitro*-m-*phenetidine*, citron-yellow, felted needles, m. p. 169—170°. If the hydrolysis is carried out in sulphuric acid the product is a mixture of dinitro-*m*-phenetidine and 4:6-dinitro-*m*-aminophenol, m. p. 231° (compare Meldola, T., 1906, **89**, 927).

W. G.

Oxidation of Phenols with Unsaturated Side Chains by means of Ozone. C. HARRIES and HANS ADAM (*Ber.*, 1916, **49**, 1029—1034. Compare A., 1915, i, 133).—Homovanillin methyl ether, the product of the reduction of eugenol methyl ether ozonide, has b. p. 121°/0·35 mm., D_{20}^{20} 1·155, n_D^{20} 1·54257, n_α 1·53905, n_β 1·55761, and the semicarbazone has m. p. 163° and the *p*-nitrophenylhydrazone m. p. 159°.

Safrole ozonide yields homopiperonaldehyde, b. p. 137°/10 mm., D_{20}^{20} 1·2626, $n_D^{20\cdot5}$ 1·55293, n_α 1·54740, n_β 1·56701; semicarbazone, m. p. 179—180°; oxime, m. p. 115° (these constants differ considerably from those recorded by Semmler and Bartelt, A., 1908, i, 901).

Chavicol methyl ether ozonide yields homoanisaldehyde, $OMe\cdot C_6H_4\cdot CH_2\cdot CHO$; b. p. 78—79°/1·5 mm., 117·5—118°/9 mm., D_4^{20} 1·096, n_D^{20} 1·53593, n_α 1·53074, n_β 1·54900, n_γ 1·56057; *semicarbazone*, silky needles, m. p. 175—176°; *phenylhydrazone*, pale yellow leaflets, m. p. 95°.

Myristicin ozonide, $C_{11}H_{12}O_3,3O_3$, and *apiole ozonide*, $C_{12}H_{14}O_4,2O_3$, could not be reduced to aldehydes. J. C. W.

***m*-Tolyl Tellurium Compounds.** KARL LEDERER (*Ber.*, 1916, **49**, 1071—1076).—Tellurium dibromide was treated with magnesium *m*-tolyl bromide, the resultant ditelluride was heated with copper powder at 270°, and then *di*-m-*tolyl telluride*, $Te(C_6H_4Me)_2$, was obtained by distillation, as a pale yellow oil, b. p. 205—206°/18 mm., which was purified by conversion into the dibromide and reduction with magnesium methyl iodide. The following *di*-m-*tolyltelluronium* compounds were prepared: *dichloride*, $(C_6H_4Me)_2TeCl_2$, needles, m. p. 131—132°; *dibromide*, scales, m. p. 165—166°; *diiodide*, shimmering, golden-orange leaflets, m. p. 164° (decomp.); *oxide*, $(C_7H_7)_2TeO$, m. p. 163—164° (crystallised from benzene), 155—156° (from xylene). The telluride combined directly with mercuric haloids; the *mercurichloride*, $(C_7H_7)_2Te,HgCl_2$, has m. p.

116—117°; and *mercuri-bromide* and *-iodide* are wax-like. It also yielded *di*-m-*tolylmethyltelluronium iodide*, $(C_7H_7)_2TeMeI$, four-sided columns, m. p. 121—122°, from which the *picrate*, with 5EtOH, m. p. 114—115°, and *platinichloride*, m. p. 154—155° (decomp.) were prepared.

The dichloride is partly hydrolysed by boiling water to the *compound*, $C_{14}H_{14}TeCl(OH)$, m. p. 87°. J. C. W.

p-Anisyl Tellurium Compounds. KARL LEDERER (*Ber.*, 1916, **49**, 1076—1082).—It was recently suggested (this vol., i, 208) that compounds supposed to be di-*p*-anisyl tellurides (Rust, Rohrbaech) were really methylene compounds. The true di-*p*-anisyl compounds have now been prepared by the author's general method.

Di-p-*anisyl telluride*, $Te(C_6H_4{\cdot}OMe)_2$, forms pearly leaflets, m. p. 56—57°, b. p. 237—243°/14 mm., and yields the following *telluronium* compounds: *dichloride*, four-sided columns, m. p. 183—184°; *dibromide*; *di-iodide*, dark red lancets, m. p. 166—167°; *oxide*, slender needles, m. p. 190—191°. It combines directly with the mercuric haloids; the *mercurichloride*, $(C_6H_4{\cdot}OMe)_2Te,HgCl_2$, has m. p. 90°; the *mercuribromide*, m. p. 77—78°, and the *mercuri-iodide*, m. p. 63°. *Di*-p-*anisylmethyltelluronium iodide* has m. p. 108—109°, and the *picrate*, $(C_7H_7O)_2TeMe,C_6H_2O_7N_3$, crystallises in slender needles, m. p. 153—154°. J. C. W.

Action of Nitric Acid on Aromatic Tellurides. KARL LEDERER (*Ber.*, 1916, **49**, 1082—1085).—Aromatic tellurides are oxidised by nitric acid (D 1·2) to the telluronium dinitrates, which are hydrolysed by water to the basic nitrates, usually obtainable as anhydrides, or even to the oxides, thus: $3TeR_2 + 2HNO_3 = 3TeR_2O + 2NO + H_2O$; $TeR_2O + 2HNO_3 = H_2O + TeR_2(NO_3)_2$; this $+ H_2O \longrightarrow OH{\cdot}TeR_2{\cdot}NO_3 \longrightarrow O(TeR_2{\cdot}NO_3)_2$.

Diphenyltelluronium dinitrate crystallises in prismatic columns, m. p. 160°, and the *anhydro-basic nitrate*, $(TePh_2{\cdot}NO_3)_2O$, in stout prisms, m. p. 223—224°. *Di*-o-*tolyltelluronium dinitrate* forms lancets or short rods, and *basic di*-p-*tolyltelluronium nitrate*, $OH{\cdot}Te(C_7H_7)_2{\cdot}NO_3$, has m. p. 237—238°. J. C. W.

Steric Hindrance with Tertiary Aromatic Amines. II. J. VON BRAUN (*Ber.*, 1916, **49**, 1101—1110. Compare A., 1913, i, 1333).—Some more examples of unexpected steric influences among the tertiary aromatic amines and the corresponding *p*-*tert.*-aminobenzyl alcohols are discussed.

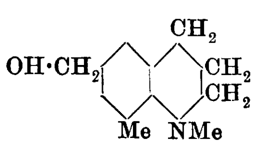
The author has shown that *tert.*-amines condense with formaldehyde to form the *p*-substituted benzyl alcohols. The yields of these products, when *o*-methyl-, chloro-, bromo-, and methoxy-dimethylanilines are heated with ten molecular proportions of formaldehyde for one hundred hours on the water-bath are found to be 6%, 36%, 45%, and 60% respectively. The reactivity towards benzaldehyde, which is extremely small, but comparable by further production of the malachite-greens, is practically nil with the first two bases, but discernible with the others. Similarly, the reaction with

methyl iodide under comparative conditions gave as the yields of the quaternary iodides, 7·6% (m. p. 209°), 15·6% (m. p. 152°), and 16% (m. p. 159°) for the first three, whilst *o*-methoxydimethylaniline reacts vigorously and completely. It might be expected that these influences of ortho-substituents would disappear in the case of the oxidation of the benzyl alcohols to acids, the alcohol group being extra-nuclear. It has been shown that this oxidation can be effected by prolonged treatment with formaldehyde (this vol., i, 474). Comparing the amounts of the bases recovered after heating them for some days with formaldehyde and hydrochloric acid and extracting the alkalinated liquid with ether, it is found that the extent of the oxidation rises from 5% to more than 36% in the four cases. This remarkable fact suggests, as the colour of these alcohols does, that the $-NMe_2$ and $-CH_2{\cdot}OH$ groups mutually influence one another in some way that our valency formulæ do not explain.

o-Bromodimethylaniline was oxidised to m-*bromo*-p-*dimethylaminobenzyl alcohol*, $NMe_2{\cdot}C_6H_3Br{\cdot}CH_2{\cdot}OH$, a yellow oil, b. p. 190—192°, which formed a *platinichloride*, m. p. 160°, and a *picrate*, m. p. 175°. Dimethyl-*o*-anisidine yielded p-*dimethylamino*-m-*methoxybenzyl alcohol*, as a yellow oil, b. p. 173—175°/17 mm., which gave a *picrate*, m. p. 154°, a *platinichloride*, and a *methiodide*, m. p. 155—156°.

The reactivity of the hydrogen in the position -6 of kairoline is comparable with that of the para-hydrogen atom in dimethylaniline. This has been known for some time for the action of nitrous acid, and was recently demonstrated for the oxidation by formaldehyde (this vol., i, 421). The linking of the trimethylene chain into a ring seemed, therefore, to have less steric influence than the presence of free ortho-substituents. Consequently, it was expected that 8-methylkairoline would be more reactive than *m*-2-dimethylxylidine, and rather like dimethyl-*o*-toluidine, whilst 6-methylkairoline would be more active than *m*-6-dimethylxylidine and similar to dimethyl-*p*-toluidine. Strange to say, instead of being about as reactive as the toluidines, these kairolines are much more reactive. The introduction of the hydrogenated quinoline ring actually increases the reactivity of the nitrogen atom and of the hydrogen atoms in the ortho- and para-positions. This is proved by comparing the reactions with methyl iodide, formaldehyde, and benzaldehyde, as above. Again, the influence of the reduced quinoline ring on the stresses in the benzene ring cannot be explained by the usual formulæ.

8-Methylkairoline was condensed with formaldehyde to the benzyl alcohol, 6-*hydroxymethyl*-1:8-*dimethyl*-1:2:3:4-*tetrahydroquinoline* (6-*hydroxymethyl*-8-*methylkairoline*)



(annexed formula), b. p. 190—200°/20 mm. 6-Methylkairoline reacted in the same way, but more quickly and thoroughly than any *tert*.-amine so far examined, to form 8-*hydroxymethyl*-1:6-*dimethyl*-1:2:3:4-*tetrahydroquinoline*

(8-*hydroxymethyl*-6-*methylkairoline*), which separated in glistening crystals, m. p. 60°, b. p. 182—185°/16 mm., and yielded a *platinichloride*, m. p. 186°, a *picrate*, m. p. 107°, and a *methiodide*, m. p. 157°. During the preparation, some of the alcohol suffered oxidation to the corresponding acid, 6-*methylkairoline*-8-*carboxylic acid*, which formed a *platinichloride*, m. p. 211°.

6-*Chlorokairoline* was prepared by reducing the chloroquinoline methiodide with stannous chloride, and after a tedious fractionation from a trace of a de-chlorinated base, was obtained as a colourless liquid, b. p. 158—161°/15 mm. (*platinichloride* and *methiodide*, m. p. 175°; *picrate*, long needles, m. p. 125°). This, again, reacted remarkably readily with formaldehyde, giving a 40% yield of 6-*chloro*-8-*hydroxymethylkairoline*, brilliant prisms, m. p. 59°, b. p. 205—210°/18 mm. (*platinichloride*, m. p. 190°; *picrate*, m. p. 117°; *methiodide*, m. p. 160°), and a 60% yield of the corresponding acid. J. C. W.

The Chloralide of Cholesterol. ADOLFO GONZÁLEZ (*Anal. Fis. Quim.*, 1916, **14**, 276—279).—Equimolecular proportions of chloral and cholesterol unite to form a *compound*, $C_{27}H_{45}\cdot OH,CCl_3\cdot CHO$, m. p. 138°, $[\alpha]_D^{21^\circ} = -27\cdot12°$. A. J. W.

The Perkin Reaction. New Method of Preparation of Substituted Cinnamic Acids. S. REICH and P. CHASKELIS (*Bull. Soc. chim.*, 1916, [iv], **19**, 287—290).—Taking advantage of the fact that toluene and its derivatives can be oxidised by chromic acid in sulphuric acid solution in the presence of acetic anhydride, giving diacetates of the corresponding substituted benzaldehydes, which on saponification give the aldehydes themselves (compare Thiele and Winter, A., 1900, i, 500), the authors submit these diacetates or their aldehydes to the Perkin reaction by heating them with sodium acetate and acetic anhydride, and thus obtain substituted cinnamic acids. Thus *o*-bromotoluene gives *o*-bromobenzaldehyde or its diacetate, and thence *o*-bromocinnamic acid.

The authors consider that Perkin's reaction may be effected by two different processes: (1) In which a substance, such as sodium malonate, is used, containing a mobile hydrogen atom, and capable of reacting with an aldehyde without the aid of acetic anhydride. (2) In which the salt, such as sodium acetate, does not contain a mobile hydrogen atom, and thus requires the use of acetic anhydride. W. G.

[1-Chloroanthraquinone-2-carboxylic Acid]. Correction. F. ULLMANN (*Ber.*, 1916, **49**, 1213. Compare this vol., i, 483).—The author has been informed that certain compounds described by him have already been described in various patents of the Badische Anilin- & Soda-Fabrik. J. C. W.

Reactions of some Carboxyl Derivatives of Trimethylene [*cyclo*Propane]. DOROTHY A. HAHN (*J. Amer. Chem. Soc.*, 1916, **38**, 1517—1534).—Methyl β-anisoyl-α-phenylethylmalonate, by

treatment with bromine in chloroform, yields hydrogen bromide and an oily bromo-derivative which is converted by careful treatment with methyl-alcoholic potassium hydroxide, or, better, magnesium methoxide, mainly into a *substance*, $C_{21}H_{20}O_6$, crystals, m. p. 86°, although an isomeric *substance*, m. p. 82°, was sometimes obtained in sufficient quantity for separation. The substance, m. p. 86°, is regarded as *methyl* 2-*anisoyl*-3-*phenyl*cyclo*propane*-1 : 1-*dicarboxylate*, $\mathrm{OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH}<\begin{matrix}\mathrm{CHPh}\\ |\\ \mathrm{C(CO_2Me)_2}\end{matrix}$. It does not reduce potassium permanganate, is reduced quantitatively to methyl β-anisoyl-α-phenylethylmalonate by zinc dust and acetic acid, and can be hydrolysed under suitable conditions, yielding the *potassium methyl* salt, $C_{20}H_{17}O_6K$, colourless plates, m. p. 152°, the *methyl hydrogen ester*, $C_{20}H_{18}O_6$, colourless prisms, m. p. 162°, or the *dicarboxylic acid*, $C_{19}H_{16}O_6$, crystals, m. p. 192° (*dipotassium* salt, $C_{19}H_{14}O_6K_2$, colourless plates). *Potassium ethyl* 2-*anisoyl*-3-*phenyl*cyclo*propane*-1 : 1-*dicarboxylate*, $C_{21}H_{19}O_6K$, colourless, hexagonal prisms, obtained by treating ethyl β-bromo-β-anisoyl-α-phenylethylmalonate with alcoholic potassium hydroxide (2 mols.), yields by acidification the *ethyl hydrogen* ester, $C_{21}H_{20}O_6$, colourless, hexagonal prisms, from which the dicarboxylic acid, m. p. 192°, can be obtained.

When methyl 2-anisoyl-3-phenyl*cyclo*propane-1 : 1-dicarboxylate is added to methyl-alcoholic magnesium methoxide and the solution is acidified, an isomeric *substance*, $C_{21}H_{26}O_6$, slender needles, m. p. 82° (*sodium* derivative, yellow needles), is obtained which reduces potassium permanganate, and is regarded as *methyl anisoylbenzylidenemethylmalonate*,

$$\mathrm{CHPh{:}C(CO{\cdot}C_6H_4{\cdot}OMe){\cdot}CH(CO_2Me)_2}.$$

This is the labile form. The stereoisomeric, stable *ester*, large prisms, m. p. 112°, is obtained by exposing to sunlight the labile ester dissolved in ether containing a little iodine, or by treating this ester or the ester, m. p. 86°, with methyl-alcoholic magnesium methoxide; it forms a *potassium* derivative, $C_{21}H_{19}O_6K$, yellow needles.

By hydrolysis with alcoholic potassium hydroxide and subsequent acidification, the esters, m. p. 82° and 112°, yield a yellow oil, from which three acids have been isolated: (1) 2-anisoyl-3-phenyl*cyclo*propane-1 : 1-dicarboxylic acid; (2) β-*anisoylpropionic acid*, $\mathrm{OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H}$, hexagonal prisms, m. p. 147° (which was also synthesised from anisole, succinic anhydride, and aluminium chloride in the presence of carbon disulphide); and (3) β-*anisoyl*-β-*benzylidenepropionic acid*,

$$\mathrm{CHPh{:}C(CO{\cdot}C_6H_4{\cdot}OMe){\cdot}CH_2{\cdot}CO_2H},$$

hexagonal prisms, m. p. 124°, which was also synthesised by hydrolysing the condensation product of benzaldehyde and ethyl β-anisoylpropionate.

When heated at about 210°, 2-anisoyl-3-phenyl*cyclo*propane-1 : 1-dicarboxylic acid evolves carbon dioxide and yields decomposition products, of which four have been isolated: (1) α-*benzyl*-

idene-γ-anisylcrotonolactone, $CH\begin{cases}C(:CHPh)\text{——}CO \\ C(C_6H_4\cdot OMe)\cdot O\end{cases}$, yellow crystals, m. p. about 173°; (2) an isomeric (stereoisomeric ?) *lactone*, green crystals, m. p. about 176°; (3) β-anisoyl-β-benzylidenepropionic acid; and (4) a small quantity of an isomeric *acid*, m. p. 124°. The two lactones were also synthesised from sodium β-anisoylpropionate, benzaldehyde, and acetic anhydride at 110—115°. By crystallisation from all solvents about one-third of the green lactone changes into the yellow lactone. Both by hydrolysis yield *β-anisoyl-α-benzylidenepropionic acid*,

$$CHPh:C(CO_2H)\cdot CH_2\cdot CO\cdot C_6H_4\cdot OMe,$$

hexagonal prisms, m. p. 165°. C. S.

The Isomerism of the Oximes. VIII. Carbanilino- and Carbethoxy-derivatives of the Oximes and the Mechanism of Isomeric Change in the Oximes and their Derivatives. Oscar Lisle Brady and Frederick Percy Dunn (T., 1916, **109**, 650—681; compare T., 1913, **103**, 1613).—Goldschmidt and van Rietschoten (A., 1893, i, 707, 709) have described three isomeric carbanilino-*m*-nitrobenzaldoximes, m. p. 105°, 139°, and 75° respectively, the existence of which they explained by assuming *cis-trans* isomerism at the second nitrogen atom; but according to such a hypothesis there should be a fourth isomeride, of which, however, no evidence is forthcoming. As the present authors have observed that the *o*-, *m*-, and *p*-carbanilino-oxybenzaldehydes (see below) decompose when heated with alcohol, the question arose as to whether the supposed existence of a third isomeric carbanilino-*m*-nitrobenzaldoxime might not be due to the acceptance of an impure substance as an isomeride. Careful investigation has proved the justification of this doubt. Not only must the isomeride described as having m. p. 139° have been impure, the correct m. p. being 148°, but the supposed isomeride, m. p. 105°, is a mixture of the two other isomerides, together with a little diphenylcarbamide and *m*-nitrobenzaldoxime; in accordance with this view, the mixture, m. p. 105°, undergoes spontaneous decomposition in a few days, forming the decomposition products of the *syn*-isomeride, m. p. 75°, namely, aniline, diphenylcarbamide, *m*-nitrobenzonitrile, and the corresponding carbanilino*anti*-aldoxime, m. p. 148°. This decomposition is typical of the carbanilino*syn*aldoximes. It was not found possible to isolate the carbanilino-*m*-nitrobenz*syn*aldoxime in a pure condition from the mixture, and the presence of this substance could only be proved by the formation of its decomposition products, but the presence of the *anti*-isomeride could be demonstrated by extraction with chloroform. The compounds m. p. 75° and 148° respectively, on hydrolysis with sodium hydroxide, yield a mixture of diphenylcarbamide, aniline, and *m*-nitrobenzonitrile, and a mixture of aniline with *m*-nitrobenz*anti*aldoxime.

The formation of a carbanilinobenz*syn*aldoxime by the action of phenylcarbimide on an *anti*aldoxime is especially noteworthy,

because Beckmann (A., 1891, 193) observed a similar rearrangement with benz*anti*aldoxime, but wrongly attributed the result to the impurity of his materials. Further investigation by the authors has led to the discovery of such isomerisation also with other *anti*aldoximes; thus the product of the interaction of phenylcarbimide and *p*-dimethylaminobenz*anti*aldoxime in ethereal solution at the ordinary temperature is mainly carbanilino-*p*-dimethylaminobenz*syn*aldoxime, m. p. 117°, with a small quantity of the *anti*-isomeride, m. p. 152°, the former isomeride undergoing conversion into the latter when boiled with alcohol or kept for some time. Also, the interaction of 3:4-dimethoxybenz*anti*aldoxime and phenylcarbimide gives rise to a mixture of *carbanilino*-3:4-*dimethoxybenz*anti*aldoxime*, needles, m. p. 129°, with the syn-*isomeride*, the latter undergoing decomposition into the *anti*-form rather less readily than in other cases. A re-examination of the behaviour of the benzaldoximes towards phenylcarbimide has shown that benz*anti*aldoxime in ethereal solution gives first a deposit of carbanilinobenz*syn*aldoxime, followed by a mixture of this with the *anti*-isomeride, whilst benz*syn*aldoxime also yields carbanilinobenz*syn*aldoxime, the m. p. of which is 77° (Beckmann, *loc. cit.*, gives 74°). Carbanilinobenz*syn*aldoxime is decomposed by boiling with alcohol, the products being aniline, diphenylcarbamide, and benzonitrile, but when recrystallised several times from benzene, it is converted into the *anti*-isomeride, m. p. 136°. The additional isomeride, m. p. 94°, described by Goldschmidt was probably a mixture of the two isomerides.

The claim of Goldschmidt that phenylcarbimide is a valuable reagent for the determination of the configuration of oximes is thus not justified, because the action of this substance on the *anti*oximes yields a certain quantity of the carbanilino*syn*-derivative, if, indeed, this is not the primary product of the reaction. On hydrolysis the carbanilino*syn*-derivatives yield nitrile, aniline, and a small quantity of diphenylcarbamide, whereas their *anti*-isomerides give the *anti*oxime, aniline, and carbon dioxide.

o-Nitrobenz*anti*aldoxime behaves in an exactly similar way to the *m*-nitro-compound towards phenylcarbimide; the compound described in the literature as carbanilino-*o*-nitrobenz*anti*aldoxime, m. p. 88°, must have been a mixture of the two isomerides, the pure compound having m. p. 117°, which agrees with the general rule that the carbanilino*anti*oximes have higher m. p.'s than the corresponding ortho-isomerides.

Ethyl chlorocarbonate appears to behave in an analogous manner to phenylcarbimide. With *p*-nitrobenz*anti*aldoxime the first product of the reaction in alkaline solution is *carbethoxy*-p-*nitrobenz*syn*aldoxime*, $NO_2\cdot C_6H_4\cdot CH:NO\cdot CO_2Et$, pale yellow needles, m. p. 94°, which when heated with alcohol for a short time is converted into the anti-*isomeride*, needles, m. p. 109°. On hydrolysis the carbethoxy-*p*-nitrobenz*syn*aldoxime gives *p*-nitrobenzonitrile, but no *p*-nitrobenz*anti*aldoxime, whereas the *anti*-isomeride yields no nitrile or ammonia, but only *p*-nitrobenz*anti*-aldoxime.

With *m*-nitrobenz*anti*aldoxime and *p*-dimethylaminobenz*anti*-aldoxime respectively the action of ethyl chlorocarbonate in alkaline solution yielded only *carbethoxy*-m-*nitrobenz*anti*aldoxime*, colourless laminæ, m. p. 97°, and *carbethoxy*-p-*dimethylamino-benz*anti*aldoxime*, colourless plates, m. p. 118°, the failure to isolate *syn*-derivatives probably being due to the rapidity of isomerisation.

An examination of the behaviour of the benzaldoximes towards hydrogen chloride confirmed the results of Luxmoore (T., 1896, **69**, 183), and also revealed the existence of a third *hydrochloride*, m. p. 103°, obtained when benz*syn*aldoxime is treated with liquid hydrogen chloride. This product, on treatment with sodium carbonate solution yielded an oil consisting largely of benz*syn*-aldoxime and very little of benz*anti*aldoxime, whereas the isomeric hydrochloride, m. p. 105°, regarded by Luxmoore as benz*anti*-aldoxime hydrochloride, when treated with sodium carbonate solution gives a mixture of the two benzaldoximes in which the *anti*-compound greatly preponderates. The hydrochlorides, m. p. 105° and 103°, are regarded respectively as the true *anti*- and *syn*-hydrochlorides, whilst in the compound, m. p. 63°, the addition of hydrogen chloride is considered to have occurred at the $>C\colon N\cdot$ linking.

The three hydroxybenzaldehydes were converted by phenyl-carbimide into the three corresponding *carbanilino-oxybenz-aldehydes*, $NHPh\cdot CO_2\cdot C_6H_4\cdot CHO$: *ortho*-compound, colourless needles, m. p. 133°; *meta*-compound, needles, m. p. 158—160°; and *para*-compound, needles, m. p. 136°; the last-named when heated with alcohol for several hours underwent decomposition, giving *p*-hydroxybenzaldehyde and diphenylcarbamide. When the sodium derivative of *p*-hydroxybenzaldehyde was treated with diphenyl-carbamyl chloride for an hour, p-*diphenylcarbamyloxybenz-aldehyde*, $NPh_2\cdot CO_2\cdot C_6H_4\cdot CHO$, was obtained as colourless needles, m. p. 100°, which slowly become blue; this aldehyde yielded an *oxime*, $NPh_2\cdot CO_2\cdot C_6H_4\cdot CH\colon N\cdot OH$, needles, m. p. 140° (*acetyl* derivative, crystals, m. p. 134°). *Dicarbanilino*-m- and -p-*oxybenz-aldoximes*, $NHPh\cdot CO_2\cdot C_6H_4\cdot CH\colon N\cdot CO_2\cdot NHPh$, were each obtained by the action of phenylcarbimide on the ethereal solution of the corresponding oxime; the *meta*-compound formed prisms, m. p. 158—160°, whilst the *para*-compound consisted of crystals, m. p. 145°. By treating a solution of *p*-hydroxybenzaldoxime and two equivalents of sodium ethoxide in alcohol with two equivalents of diphenylcarbamyl chloride, *diphenylcarbamyl*-p-*diphenylcarbamyl-oxybenzaldoxime*, $NPh_2\cdot CO_2\cdot C_6H_4\cdot CH\colon N\cdot CO_2\cdot NPh_2$, colourless crystals, m. p. 162°, was produced.

The authors submit to review the various reactions of the oximes and demonstrate that in almost every case an assumption of the tautomerism of the oximes is sufficient to account for the observed facts; the spontaneous conversion of the *syn*oximes and some of their derivatives into the corresponding *anti*-compounds is explained by an intermediate polymerisation into double molecules (compare Stewart, P., 1905, **21**, 73). D. F. T.

Benzyl Methyl Ketone and Phenylsulphonal. AKIRA OGATA and CHUJIRO ITO (*J. Pharm. Chim.*, 1916, [vii], **14**, 148—150; from *Yakugakuzasshi*, 1916, **409**).—α-Phenylacetoacetonitrile, COMe·CHPh·CN, when dissolved in concentrated sulphuric acid and the solution poured into water, gives *α-phenylacetoacetamide*, COMe·CHPh·CO·NH_2, which occurs in a stable form, prisms, m. p. 131°, and an unstable form, small granular crystals, m. p. 117—119°, the latter readily passing into the former by heating it at 119° or recrystallising it. The amide when boiled with 15% sulphuric acid loses ammonia and carbon dioxide, and is converted into benzyl methyl ketone. When this ketone is condensed with ethyl mercaptan under the influence of hydrogen chloride the product is *benzylmethylketoethylmercaptol*, a yellow liquid, b. p. 250—254°, which when oxidised with a 5% solution of potassium permanganate gives *phenylsulphonal*, CH_2Ph·$CMe(SO_2Et)_2$, colourless, odourless, insipid prisms, m. p. 125·5°. W. G.

Condensation of Aldehydes with Ketones. II. Aldehydes with Methyl Ethyl Ketone. HUGH RYAN and ANNIE DEVINE (*Proc. Roy. Irish Acad.*, 1916, **32**, [*B*], 208—216).—In 1902 Harries and Müller showed that methyl ethyl ketone condenses with benzaldehyde in the presence of alkali to form the α-benzylidene derivative, CHPh:CH·COEt (previously prepared and described by Levinstein as the γ-derivative), and in the presence of hydrochloric acid to form the γ-benzylidene derivative, COMe·CMe:CHPh; also that the α-derivative condenses further with benzaldehyde to form a pyrone derivative, $C_{18}H_{18}O_2$, m. p. 68·5° (oxime, m. p. 195—196°). On repeating the experiments of Harries and Müller the authors obtained the α-benzylidene derivative (styryl ethyl ketone) from benzaldehyde and methyl ethyl ketone in the presence of dilute aqueous sodium hydroxide, but by the continued action of benzaldehyde they obtained, not the substance, m. p. 68·5°, but an isomeric *substance*, $C_{18}H_{18}O_2$ (or possibly the same substance in a purer form), m. p. 81—83°, which formed an oxime, m. p. 195—196°, *phenylhydrazone*, m. p. 134°, and *semicarbazone*, m. p. 195—198°. This substance is regarded as an unsaturated ketone rather than as a pyrone derivative, because it develops an orange coloration with concentrated sulphuric acid. When it, or styryl ethyl ketone, or methyl ethyl ketone is treated with benzaldehyde and alcoholic hydrogen chloride, a *substance*, $C_{25}H_{20}O$, short, rectangular prisms, m. p. 156°, is obtained (*dibromide*, $C_{25}H_{20}OBr_2$, rectangular prisms, m. p. 145° [decomp.]), the structure of which has not yet been elucidated. With the same condensing agent styryl ethyl ketone yields analogous *compounds*, $C_{27}H_{24}O_3$, colourless crystals, m. p. 173°, and $C_{27}H_{20}O_5$, yellow, hexagonal plates, m. p. 191°, with anisaldehyde and with piperonal respectively.

Methyl ethyl ketone and piperonal in the presence of alcoholic hydrogen chloride condense to form a blue solid (? oxonium salt), which yields by treatment with alkali a *substance*, $C_{28}H_{20}O_7$, colourless, rectangular prisms, m. p. 212°. C. S.

Transformation of Nopinone. ENRICO RIMINI (*Gazzetta*, 1916, **46**, ii, 119—121).—The transformation which certain bicyclic ketones undergo when treated with sulphuric acid is, apart from varying yields, the same with the hot dilute acid as with the cold concentrated acid. When boiled with dilute sulphuric acid, nopinone gives 1-*iso*propyl-Δ^2-*cyclo*hexen-4-one alone, whilst the action of the cold concentrated acid gives, in addition, 1-*iso*propylidene-4-*cyclo*hexanone. T. H. P.

Benzoylphenylethylene Oxide. Postscript. OSKAR WIDMAN (*Ber.*, 1916, **49**, 1023. Compare this vol., i, 406).—In reviewing the chemistry of the isomerides of dibenzoylmethane, the author overlooked the fact that Ruhemann and Watson (T., 1904, **85**, 456) had shown that Löwenheim's supposed dibenzoylmethane was really ethoxybenzylideneacetophenone. The diketone, as such, is still unknown. J. C. W.

Configuration of Certain Glyoximes. A. ANGELI (*Atti. R. Accad. Lincei*, 1916, [v], **25**, ii, 7—15).—The author discusses the different configurations which have been ascribed to peroxides of the glyoximes. Contrary to the statement of Wieland and Semper (A., 1908, i, 108), he finds that these peroxides react readily with Grignard's reagent, in either ethereal or benzene solution. With piperylmethylglyoxime peroxide and magnesium phenyl bromide the products of the reaction consist principally of piperonylonitrile, acetophenone, and a new ketone which resembles benzophenone and is undoubtedly of the form $CH_2O_2{:}C_6H_3{\cdot}COPh$. The water resulting from the treatment of the product with ice gives Konovalov's reaction for nitro-derivatives, and appears to contain the salt of a nitronic acid, $CMePh{:}NO{\cdot}OH$, which would be readily decomposable by acid, yielding partly the isomeric nitro-derivative and partly the isomeric green nitroso-alcohol, $OH{\cdot}CMePh{\cdot}NO$, this in its turn giving acetophenone. The new ketone (*vide supra*) probably arises from the piperonylonitrile by further action of the magnesium phenyl bromide, Blaise having shown that nitriles readily yield ketonic compounds under such treatment.

These results are not in agreement with the views of Wieland and Semper (*loc. cit.*) on the structure of the peroxides, but support the formulæ attributed to these compounds by Green and Rowe (T., 1913, **103**, 897).

To benzildioxime, which is obtainable by reduction of its peroxide, Beckmann (A., 1893, i, 474) ascribed the configuration $\begin{array}{l}Ph{\cdot}C\text{———}C{\cdot}Ph\\ \quad\;\| \qquad\quad \|\\ \;\;N{\cdot}OH \quad N{\cdot}OH\end{array}$, since it yields benzoylphenylcarbamide, $NHPh{\cdot}CO{\cdot}NHBz$, when treated with phosphorus pentachloride. The latter is, however, a very energetic reagent and, further, chlorinated products are probably formed as intermediate products in this reaction, and these may have structures different from that of the starting product. If Beckmann's transposition is to be employed to determine the configurations of the glyoximes, the manner in which this transposition proceeds must first be definitely

established, since the study of ethylenic compounds shows that intramolecular reactions in the *cis*-position are not always preferred.

Diacetyldioxime undoubtedly has the configuration,

$$\begin{array}{lcl} \mathrm{Me{\cdot}C} & \text{———} & \mathrm{C{\cdot}Me} \\ \quad \| & & \| \\ \mathrm{N{\cdot}OH} & & \mathrm{HO{\cdot}N} \end{array},$$

and dibenzoylglyoxime, $\begin{array}{lcl} \mathrm{Bz{\cdot}C} & \text{———} & \mathrm{C{\cdot}Bz} \\ \quad \| & & \| \\ \mathrm{N{\cdot}OH} & & \mathrm{HO{\cdot}N} \end{array}$, and the other oxime, $\begin{array}{llcl} \mathrm{Me{\cdot}C{-}CH_2{-}} & \mathrm{C} & \text{———} & \mathrm{C{\cdot}Me} \\ \quad \| & \| & & \| \\ \mathrm{N{\cdot}OH} & \mathrm{N{\cdot}OH} & & \mathrm{HO{\cdot}N} \end{array}$, prepared by the author (compare A., 1893, i, 310, 355), exhibit such a marked tendency to lose a molecule of water that distillation of their solutions is sufficient to transform them into the corresponding anhydrides; the above structures are therefore the only ones which can reasonably be ascribed to them. Further, the author finds that these oximes are able to furnish complex salts analogous to those discovered by Tschugaev, and for this to occur the dioximes must contain vicinal hydroxyl groups. T. H. P.

Diketones Derived from Diacetylresorcinol Dimethyl Ether. JOSEPH ALGAR (*Proc. Roy. Irish Acad.*, 1916, **33**, [*B*], 86—90).—The method of preparing diflavone by condensing diacetylresorcinol dimethyl ether (4 : 6-diacetyl-1 : 3-dimethoxybenzene) with methyl benzoate in the presence of sodium at 120° (Ryan and O'Neill, A., 1915, i, 707) has been utilised in preparing 4 : 6-*dianisoylacetyl*-1 : 3-*dimethoxybenzene*, $C_6H_2(OMe)_2(CO{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}OMe)_2$, pale yellow prisms, m. p. 232—234°, from methyl anisate, 4 : 6-*di-ω-phenylacetoacetyl*-1 : 3-*dimethoxybenzene*,

$$C_6H_2(OMe)_2(CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2Ph)_2,$$

colourless needles, m. p. 131—132°, from phenylacetic ester, 4 : 6-*diacetoacetyl*-1 : 3-*dimethoxybenzene*, $C_{16}H_{18}O_6$, colourless prisms, m. p. 116—118°, from acetic ester, and *ethyl* 4 : 6-*dimethoxy*iso*phthaloyldipyruvate*, $C_6H_2(OMe)_2(CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Et)_2$, yellow needles, m. p. 186—188°, from ethyl oxalate; the corresponding *methyl* ester, $C_{18}H_{18}O_{10}$, bright yellow needles, has m. p. 205—206°. Attempts to prepare dichromones from the third and the fourth compounds were unsuccessful. C. S.

Unsaturated β-Diketones. III. HUGH RYAN and GERALDINE PLUNKETT (*Proc. Roy. Irish Acad.*, 1916, **32**, [*B*], 199—207. Compare Ryan and Dunlea, A., 1913, i, 1067; Ryan and Algar, *ibid.*, i, 1068).—3 : 4-*Dimethoxystyryl methyl ketone*,

$$C_6H_3(OMe)_2{\cdot}CH{:}CH{\cdot}COMe,$$

almost colourless prisms, m. p. 85—86°, prepared by keeping for twelve hours a mixture of veratraldehyde, aqueous acetone, and 25% sodium hydroxide or by methylating ferulic methyl ketone, is warmed with methyl oxalate and sodium, whereby, after decomposing the resulting *sodium* derivative, *methyl αγ-diketo-ε-3 : 4-dimethoxyphenyl-Δ^δ-hexenoate*,

$$C_6H_3(OMe)_2{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Me,$$

orange-yellow plates, m. p. 121—122°, is obtained. This reacts

with hydroxylamine hydrochloride in boiling alcohol to form *ethyl 3-dimethoxystyryl*iso*oxazole-5-carboxylate*,

$$C_6H_3(OMe)_2\cdot CH{:}CH\cdot C{<}{\genfrac{}{}{0pt}{}{-CH}{N\cdot O}}{>}C\cdot CO_2Et,$$

colourless prisms, m. p. 135—137°, the methyl ester having been converted into an ethyl ester. *αγ-Diketo-ε-3:4-dimethoxyphenyl-Δ^δ-hexenoic* (3:4-*dimethoxycinnamoylpyruvic*) *acid* forms orange-red prisms, m. p. 185°. Its methyl ester in cold alcohol condenses with aqueous benzenediazonium chloride in the presence of sodium acetate to form *methyl β-benzeneazo-αγ-diketo-ε-3:4-dimethoxyphenyl-Δ^δ-hexenoate*,

$$C_6H_3(OMe)_2\cdot CH{:}CH\cdot CO\cdot CH(N{:}NPh)\cdot CO\cdot CO_2Me,$$

orange needles, m. p. 105—107°, which is soluble in dilute aqueous potassium hydroxide.

3:4-Methylenedioxystyryl methyl ketone and methyl oxalate heated with sodium yield *methyl αγ-diketo-ε-3:4-methylenedioxyphenyl-Δ^δ-hexenoate*, $C_{14}H_{12}O_6$, yellow plates, m. p. 174°. The free *acid* crystallises in orange-red needles, m. p. about 185° (decomp.).

The shades produced on mordanted wool by the unsaturated diketones described above and previously (*loc. cit.*) are compared with those produced by turmeric. C. S.

Stereochemistry of Quinone Oximes. VIII. Constitution of the Chlorotoluquinone Oximes prepared by Oliveri-Tortorici from *o*- and *m*-Cresol. F. KEHRMANN [with ST. HEMPEL] (*Ber.*, 1916, **49**, 1211—1213).—Nitroso-*o*- and -*m*-cresols were found to combine with chlorine to form dichlorides, from which alcohol eliminated the elements of hydrogen chloride (A., 1898, i, 303). The position of the remaining chlorine atom in each case was left undecided. The question has now been answered by reducing the compounds to the chloroaminocresols and oxidising these again to the known chlorotoluquinones (compare this vol., i, 210). It appears that the compound, m. p. 158—159°, derived from *o*-cresol is 3-chloro-2:5-toluquinone-5-oxime, and the "chloronitrosocresol" from *m*-cresol, m. p. 147—148°, is 4-chloro-2:5-toluquinone-2-oxime. J. C. W.

Preparation of 5-Nitro-1-alkylaminoanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 292395; from *J. Soc. Chem. Ind.*, 1916, **35**, 830).—5-Nitro-1-alkylaminoanthraquinones are obtained by nitrating *α-N*-acidylalkylaminoanthraquinones. G. F. M.

Preparation of Anthraquinone α-Mercaptans and Disulphides. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 292457; from *J. Soc. Chem. Ind.*, 1916, **35**, 830).—Anthraquinone α-mercaptans and disulphides are obtained by the reduction of anthraquinone α-sulphochlorides or the corresponding sulphinic acids with hyposulphites. G. F. M.

Preparation of Thiocarbamides of the Anthraquinone Series. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P., 291984; from *J. Soc. Chem. Ind.*, 1916, **35**, 830).—Thiocarbamides of the anthra-

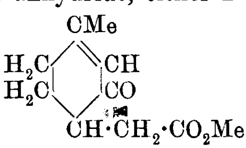
quinone series are prepared by heating 2-aminoanthraquinone or its ring substitution products with an alkali xanthate in an organic solvent of high boiling point. G. F. M.

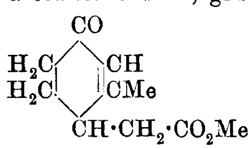
Hydrochloride and Hydrobromide of *d*-Pinene. *d*-Camphene (Austracamphene). D. E. TSAKALOTOS and B. PAPACONSTANTINOU (*J. Pharm. Chim.*, 1916, **14**, 97—103).—According to Wallach, lævo-rotatory essence of turpentine yields the *l*-hydrochloride and hydrobromide of pinene, whereas the dextro-rotatory essence gives inactive preparations. Essence of Grecian turpentine is almost pure *d*-pinene, and from samples with b. p. 155—156°/760 mm. the authors have now prepared the *d*-hydrochloride and hydrobromide of pinene.

The d-*hydrochloride* has m. p. 127·1° (Raoult's apparatus), b. p. 207°/750 mm., $[\alpha]_D^{17}$ +33·19°; the d-*hydrobromide* has m. p. 80°, $[\alpha]_D^{21}$ +31·31°, and decomposes before boiling.

By the action of potassium phenoxide on the above hydrochloride the authors have also prepared d-*camphene*, m. p. 42·7°, b. p. 157·6°/745 mm., $[\alpha]_D^{28}$ +84·05°. J. C. W.

Oxidation of Limonene by Ozone. C. HARRIES and HANS ADAM (*Ber.*, 1916, **49**, 1034—1036).—Limonene diozonide yields on oxidation with chromic acid and glacial acetic acid, βδ-*diacetylvaleric acid*, a viscous syrup, which suffers loss of water and consequent ring formation, when warmed with dilute alkali hydroxide or when treated with methyl-alcoholic hydrogen chloride. The ester of the anhydride, either I or II, forms a *semicarbazone*, glistening


(I.)


(II.)

leaflets, m. p. 173—174°, a *phenylhydrazone*, golden-yellow leaflets, m. p. 135° (decomp.), and a p-*nitrophenylhydrazone*, yellowish-brown needles, m. p. 173°. The ozonide can also be converted into the same acid by heating with *N*-potassium hydroxide, but in this case a volatile neutral oil is also formed. J. C. W.

Volatile Oil of Calycanthus Occidentalis. CHARLES C. SCALIONE (*J. Ind. Eng. Chem.*, 1916, **8**, 729—731).—The spice bush, *Calycanthus occidentalis* or *Butneria occidentalis*, grows in Northern California and Southern Oregon. The leaves and twigs of the shrub yield about 0·27% of volatile oil, which has D^{25} 0·9295, $[\alpha]_D$ +7·46°, n_D^{20} 1·4713, saponification number, 54·3, acetyl number, 33·5. The oil has a greenish-yellow colour, a bitter taste, and a camphoraceous odour: it is soluble in all proportions in 90% alcohol and in 16 vols. of 70% alcohol (by vol.). The composition of the oil is: *d*- and *l*-pinene, 8·30%; cineol, 60·32%; borneol, 9·21%; linalyl acetate, 18·99%; small quantities of camphor, methyl salicylate, and sesquiterpene alcohols are also present. W. P. S.

The Essential Oil of Cinnamomum Oliveri (Bail.) or Brisbane Sassafras. GEORGE WATSON HARGREAVES (T., 1916, **109**, 751—754).—The bark and leaves of the *Cinnamomum Oliveri* were separately distilled in a current of steam, and the resulting oils were separated into their respective constituents by fractional distillation. The oil from the bark consisted of pinene (12—15%), *d*-camphor (18—20%), safrole (25—27%), and eugenyl methyl ether (40—45%). The oil from the leaves contains a mixture of terpenes (25%), consisting mainly of pinene with a trace of phellandrene, *d*-camphor (60%), and phenols and other substances (15%). These results differ widely from those obtained by Smith (compare Baker, *Proc. Linn. Soc. N.S.W.*, 1897, ii, 275), but the figures for the bark oil are in moderate agreement with those obtained by Scott (T., 1912, **101**, 1612) for the oil from the leaves of *Athenosperma moschatum* (Australian sassafras, native of Victoria). W. G.

The Vulcanisation of Caoutchouc and the Possibility of its Regeneration from "Vulcanisates." I. C. HARRIES (*Ber.*, 1916, **49**, 1196—1201).—Between the purely chemical theories and the colloid-chemical views of the vulcanisation of caoutchouc, there are important compromises. It is known that about 2—4% of the sulphur in a vulcanite is very firmly fixed, so that Axelrod, Alexander, and Hinrichsen and Kindscher (1910) have regarded this part at least as chemically combined. With the advantageous co-operation of technical experts, the author is able to throw some new light on the problem.

Hinrichsen and Kindscher performed their experiments with sulphur chloride on so-called "purified" caoutchouc, and it is now recognised that although this is chemically comparable with natural caoutchouc, it has acquired quite different colloidal properties by the process of reprecipitation. The difference needs to be emphasised. The ordinary hot vulcanisation, as adapted to the preparation of rubber tyres, has been investigated more closely. It is recognised that there is a primary vulcanisation and an after-vulcanisation, which can be catalysed by means of lead oxide (Seidl, 1911). The first process is now shown to be purely an adsorption phenomenon, for the sulphur can be completely extracted from a specimen of freshly treated natural caoutchouc, and it does not enter into the constitution of the hydrochloride. The hydrochloride obtained from a rubber that has undergone after-vulcanisation, however, does contain sulphur. Natural caoutchouc is to be regarded as a metastable substance which changes into a stable form, the vulcanisate, on vulcanisation. Consequently, other substances than sulphur should bring about this process. The change is not entirely a colloidal one, for the hydrochlorides of natural caoutchouc and of a de-sulphurised vulcanisate are different, and the latter reacts much more slowly with ozone and is less soluble in carbon disulphide. Moreover, the vulcanisate cannot be vulcanised again by the hot treatment; at least, the product is never again so elastic. Only the metastable, natural caoutchouc has the necessary colloidal characteristics ("emulsoid" form) for the production

of a really good rubber, and the great problem of the regeneration of caoutchouc is not the extraction of the sulphur, but the revival of the original colloidal properties. Even the amount of sulphur which is so firmly fixed during the after-vulcanisation is not of great importance, for it can scarcely be chemically combined (3% would be about 1 atom to a molecule of $C_{75}H_{120}$). J. C. W.

Synthesis of a Chlorophyll Pigment by Albert and Alexandre Mary. THÉMISTOCLE JONA (*Mon. Sci.*, 1916, [v], **6**, i, 149—150).—A destructive criticism of A. & A. Marys' claim to have synthesised crystalline chlorophyll (A., 1915, i, 979). The authors' methods and arguments are condemned as inadequate, and surprise is expressed that if they have obtained chlorophyll so easily by a simple reaction, they have not submitted the substance to examination by the well-known methods of organic analysis. C. S.

Residual Affinities of Benzopyrones. II. Double Compounds of 2 : 3-Dimethyl-4-thiochromone [2 : 3-Dimethyl-γ-benzthiopyran]. H. SIMONIS and ALFRED ELIAS (*Ber.*, 1916, **49**, 1116—1125. Compare this vol., i, 62).—Most chemists have regarded the salts of benzo-γ-pyrones as oxonium salts, but Gomberg and Cone (A., 1910, i, 872) expressed the opinion that they are not true salts, but that the addition of the acid molecule takes place at the carbonyl group. The present study of a benzthiopyran is a further contribution to this problem. 2:3-Dimethyl-γ-benzthiopyran (A., 1914, i, 712) gives a large number of compounds with metallic salts, but it differs considerably from the corresponding benzopyrone in forming no salts with the halogen hydracids. It dissolves with difficulty in concentrated hydrochloric acid and is not decomposed by this acid even when heated in a sealed tube at 100°. Even the metallic compounds precipitated from hydrochloric acid solution are mostly free from this acid (unlike the benzopyrone salts), but the compounds with uranyl and ferric chlorides contain combined acid. It is presumed that in the latter cases internal rearrangement has taken place, which is also connected apparently with unusual intensity in the colours of the salts.

Mercuric chloride gives in a hydrochloric acid solution the *compound* $(C_{11}H_{10}OS)_2,HgCl_2$, golden tablets, which changes into the green compound $C_{11}H_{10}OS,HgCl_2$ (*loc. cit.*), when digested with absolute alcohol, ether, or chloroform, and the latter reverts to the former compound on boiling with hydrochloric acid. The *compound* B_2,Cu_2Cl_2, m. p. 204°, is like graphite; the *compound* $B_2,PtCl_4$, is very dark brown; the *compound* $(BiI_3)_2B$ forms small, carmine-red needles, m. p. 192°; the *compound* $B,AuCl_3$, obtained from ethereal solutions, is almost black and has m. p. 76° (decomp.); the pale brown *compound*, $B_3,2AuCl_3$, m. p. 120—130°, is formed in acid solutions; the *compound* $B_2,UO_2Cl_2,2HCl$, m. p. 118°, is pink; the *compound* $B,FeCl_3,HCl$ is pale green, and loses the acid

and becomes dark blue when exposed to the air or kept at 80°. Precipitates were obtained with several other metallic salts.

A double *compound* with aniline, B_2,NH_2Ph, is also readily obtained in pale red needles, m. p. 92°, which are quickly decomposed by cold water. J. C. W.

Some Xanthone Derivatives and Xanthone Colouring Matters. SURENDRANATH DHAR (T., 1916, **109**, 744—750).—Certain bromo- and nitro-derivatives of xanthone have been prepared, and from these some anilino-derivatives and azo-dyes have been obtained, but their dyeing properties are of no special interest.

Bromoxanthone (compare Graebe, A., 1890, 504) is best prepared by heating xanthone and the calculated quantity of bromine with a trace of iodine in the least possible amount of nitrobenzene at 80—110° and finally at 180°. Dibromoxanthone (compare Perkin, T., 1883, **43**, 1870) can be obtained in theoretical yield by a similar modified method.

Tetrabromoxanthone is prepared either by heating xanthone (1 mol.) with bromine (4 mols.) and a trace of iodine in a sealed tube at 200—275° for six hours, or by heating either α- or β-dinitroxanthone with bromine (2—4 mols.) in a sealed tube at 275—290° for eight hours. It crystallises in white needles, m. p. 298°.

Hexabromoxanthone, $C_{13}H_2O_2Br_6$, golden-yellow needles, m. p. 308°, is obtained by heating xanthone in a sealed tube at 275° for twelve hours with a large excess of bromine and a trace of iodine.

The author has slightly modified Perkin's method (*loc. cit.*) for preparing α- and β-dinitroxanthones, thereby readily obtaining them in a pure state.

On adding bromoxanthone to a mixture of three parts of nitric acid (D 1·4) and 1·5 parts of concentrated sulphuric acid, *bromodinitroxanthone*, pale yellow needles, m. p. 235°, crystallised out after a few hours. From the filtrate and washings a much bigger yield of *bromotrinitroxanthone*, $C_{13}H_4O_2(NO_2)_3Br$, rhombohedral, yellow plates, m. p. 262—265°, was obtained.

Dibromoxanthone (1 part) was dissolved by boiling in 30 parts of nitric acid (D 1·48) and 15 parts of concentrated sulphuric acid, and, on cooling, *dibromodinitroxanthone*, $C_{13}H_4O_2Br_2(NO_2)$, was deposited in colourless needles, m. p. 235—237°.

Tetrabromoxanthone, when boiled for half-an-hour in twice the above amount of a similar acid mixture, was converted into *tetrabromodinitroxanthone*, $C_{13}H_2O_2(NO_2)_2Br_4$, rectangular plates, m. p. 300°. Attempts to prepare a nitro-derivative from hexabromoxanthone were not successful.

β-Dinitroxanthone, when reduced by alcoholic ammonium sulphide, yielded *β-nitroaminoxanthone*, $NO_2\cdot C_{13}H_6O_2\cdot NH_2$, fine, yellow needles, m. p. 265°, giving an *acetyl* derivative, m. p. above 300°. The base, when diazotised and coupled with β-naphthol, yielded *β-nitroxanthoneazo-β-naphthol*, $NO_2\cdot C_{13}H_6O_2\cdot N_2\cdot C_{10}H_6\cdot OH$, an amorphous product, m. p. above 300°, which gave orange shades

on chrome-mordanted wool. When diazotised and coupled with 1:5-dihydroxynaphthalene the base yielded *β-nitroxanthoneazo-1:5-dihydroxynaphthalene*, $NO_2\cdot C_{13}H_6O_2\cdot N_2\cdot C_{10}H_5(OH)_2$, a dark red precipitate, m. p. above 300°, which dyed chrome-mordanted wool in brown shades.

α-Dinitroxanthone, when reduced by alcoholic ammonium sulphide, gave *α-nitroaminoxanthone*, yellow needles, m. p. 204—206°, giving an *acetyl* derivative, pale yellow needles, m. p. above 300°, and *α-nitroxanthoneazophenol*, $NO_2\cdot C_{13}H_6O_2\cdot N_2\cdot C_6H_4\cdot OH$, a dark brown precipitate, m. p. above 300°, which dyed chrome-mordanted wool in yellowish-brown shades.

Dibromoxanthone heated with ten times its weight of aniline and a trace of copper powder gave a blue, crystalline *compound*, m. p. 216—218°, which was not characterised. Tetrabromoxanthone, when boiled with ten times its weight of aniline and a trace of copper powder for two hours, yielded *dibromodianilinoxanthone*, $C_{13}H_4O_2Br_2(NHPh)_2$, a bluish-black precipitate, m. p. 140—145°, which gave blue shades on chrome-mordanted wool. Hexabromoxanthone, when heated with fifteen times its weight of aniline and a trace of copper, yielded *hexa-anilinoxanthone*, $C_{13}H_2O_2(NHPh)_6$, m. p. 180—183°, giving deep blue shades on chrome-mordanted wool. α-Dinitroxanthone, when similarly treated with aniline, yielded *phenyliminodinitroxanthone*, $C_{13}H_6O(NO_2)_2\text{:}NPh$, a violet-blue powder, m. p. 170—175°, which gave pale violet shades on tannin-mordanted cotton.

Various attempts made to prepare vat dyes were unsuccessful.

W. G.

The Diflavone Group. III. Derivatives of Dicoumaranone and of Diflavanone. HUGH RYAN and JOSEPH ALGAR (*Proc. Roy. Irish Acad.*, 1916, **32**, [*B*], 185—192. Compare A., 1915, i, 707, 1701).—In connexion with the relation between the colours of members of the diflavone and the monoflavone groups it is desirable to examine derivatives of diflavone which contain auxochromes.

4:6-*Di*-p-*methoxycinnamoyl*-1:3-*dimethoxybenzene*,

$$C_6H_2(OMe)_2(CO\cdot CH\text{:}CH\cdot C_6H_4\cdot OMe)_2,$$

pale yellow needles, m. p. 204—205°, obtained by heating an alcoholic solution of 4:6-diacetyl-1:3-dimethoxybenzene and anisaldehyde with 25% sodium hydroxide on the water-bath, yields by treatment with bromine (2 mols.) in chloroform and recrystallisation of the product a *substance*, colourless needles, m. p. 166—168°, which appears to be a *dibromide*, $C_{28}H_{26}O_6Br_2$.

α-4:6-*Di*-p-*methoxycinnamoyl*-1:3-*dihydroxybenzene*, $C_{26}H_{22}O_6$, orange crystals, m. p. 205—206° (compare Eykman, Bergema, and Henrad, A., 1905, i, 359), is obtained in a similar manner from 4:6-diacetyl-1:3-dihydroxybenzene, anisaldehyde, and 50% sodium hydroxide. The *β-isomeride*, $C_{26}H_{22}O_6$, obtained from the same three substances in an aqueous medium after six months, forms yellow crystals, m. p. 195—196°. The α- or the β-compound heated with acetic anhydride and anhydrous sodium acetate forms

an oily *diacetate*. This is converted by bromine in chloroform into an amorphous *tetrabromide*, which yields *dianisylidenedicoumaranone*,

$$OMe\cdot C_6H_4\cdot CH{:}C{<}{}^{O-}_{CO}{>}C_6H_2{<}{}^{O-}_{CO}{>}C{:}CH\cdot C_6H_4\cdot OMe,$$

yellow prisms, m. p. 327—328·5°, by heating with alcoholic *N*/2-potassium hydroxide (6 mols).

6-p-*Methoxycinnamoyl*-7-*hydroxy*-4′-*methoxy*-3-*anisylideneflavanone*,

$$OMe\cdot C_6H_4\cdot CH{:}CH\cdot CO\cdot C_6H_2(OH){<}\begin{array}{l}O{-}CH\cdot C_6H_4\cdot OMe\\ CO\cdot C{:}CH\cdot C_6H_4\cdot OMe\end{array},$$

obtained by dissolving 4 : 6-diacetyl-1 : 3-dihydroxybenzene and anisaldehyde in hot alcohol, saturating the solution with hydrogen chloride, and keeping it, with occasional heating, for several days, forms orange-yellow leaflets, m. p. 243—245°, and develops in concentrated sulphuric acid a deep blue colour, changing rapidly to purple-red. *Dianisylidene*-4′ : 4″-*dimethoxydiflavanone*,

$$\begin{array}{r}OMe\cdot C_6H_4\cdot CH\cdot O\\ OMe\cdot C_6H_4\cdot CH{:}C{-}CO\end{array}{>}C_6H_2{<}\begin{array}{l}O{-}CH\cdot C_6H_4\cdot OMe\\ CO\cdot C{:}CH\cdot C_6H_4\cdot OMe\end{array},$$

yellow prisms, m. p. 249—251°, is obtained by keeping an alcoholic solution of the same two substances, saturated with hydrogen chloride, for five days. C. S.

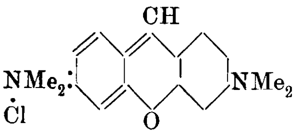
Diflavone Group. IV. Diveratrylidenedicoumaranone. Hugh Ryan and Michael J. Walsh (*Proc. Roy. Irish Acad.*, 1916, **32**, [*B*], 193—198).—4 : 6-Diacetyl-1 : 3-dimethoxybenzene and veratraldehyde in the presence of alcoholic sodium hydroxide condense on heating to form 4 : 6-*dicinnamoyl*-1 : 3 : 3′ : 4′ : 3″ : 4″-*hexamethoxybenzene*, $C_6H_2(OMe)_2(CO\cdot CH{:}CH\cdot C_6H_3[OMe]_2)_2$, pale yellow prisms, m. p. 216—217°, softening at 212°. In a similar manner, from 4 : 6-diacetyl-1 : 3-dihydroxybenzene is obtained the orange *sodium* derivative of 4 : 6-*dicinnamoyl*-1 : 3-*dihydroxy*-3′ : 4′ : 3″ : 4″-*tetramethoxybenzene*, $C_{28}H_{26}O_8$, pale orange-yellow prisms, m. p. 194—196°, the tinctorial effects of which on mordanted wool are very slight in comparison with those produced by turmeric. The *diacetate*, $C_{32}H_{30}O_{10}$, yellow prisms, m. p. 155—157°, yields by bromination in chloroform an amorphous *tetrabromide*, which is converted by heating with alcoholic *N*/2-potassium hydroxide into *diveratrylidenedicoumaranone*,

$$C_6H_3(OMe)_2\cdot CH{:}C{<}{}^{O-}_{CO}{>}C_6H_2{<}{}^{O-}_{CO}{>}C{:}CH\cdot C_6H_3(OMe)_2,$$

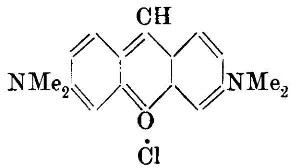
yellow plates, m. p. 285—286°. The last substance is regarded as a dicoumaranone, not as tetramethoxydiflavone, because it develops in concentrated sulphuric acid a dark violet coloration which changes to brown after a few hours. C. S.

The Para-quinonoid Constitution of Pyronin. J. von Braun and E. Aust (*Ber.*, 1916, **49**, 989—999).—It has become

customary in recent years to ascribe an ortho-quinonoid configuration to the basic derivatives of xanthen, notably pyronin, making them, therefore, structurally analogous to the safranine, oxazine, and thiazine dyes. Although it has been fairly well proved that the latter form ortho-quinonoid salts, there is no evidence that the salt formation in the former dyes is due to the oxygen atom becoming quadrivalent. It is now shown that it is much more probable that the nitrogen atom is the bearer of the acid radicle, a salt of pyronin having therefore a para-quinonoid configuration, thus:



and not



m-Hydroxydimethylaniline is converted into tetramethyldiaminoxanthen, and this is treated with cyanogen bromide, whereby 3 : 6-*dicyanodimethyldiaminoxanthen*,

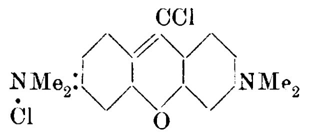
$$CN\cdot NMe\cdot C_6H_3<\substack{CH_2\\ O}>C_6H_3\cdot NMe\cdot CN,$$

is obtained as an almost colourless powder, m. p. 190—193°. This only dissolves in concentrated acids, and is very stable towards oxidising agents. It is oxidised by chromic acid to the *xanthone*, which crystallises in yellow needles, m. p. 274°, and dissolves only in concentrated acids. The oxonium chloride solution gives a yellow *ferrichloride*, m. p. 142°. The xanthone was further hydrolysed by boiling with alcoholic sodium hydroxide to 3 : 6-*dimethyldiaminoxanthone*, which has m. p. 235°, exhibits brilliant violet fluorescence in alcohol or chloroform, dissolves in concentrated sulphuric acid with sky-blue fluorescence, and gives with difficulty yellow solutions with intense green fluorescence in dilute acids. The *hydrochloride*, $C_{15}H_{15}O_2N_2Cl$, forms an orange powder, m. p. 215°; the *platinichloride* has m. p. 225°; the colourless *nitroso*-compound has m. p. 235°; the *acetyl* compound has m. p. 178°.

It was hoped to reduce the dicyanodimethyldiaminoxanthone to the xanthydrol, but this could not be accomplished without removing the cyano-groups. Had it been possible, the xanthydrol would have been compared with the tetramethyldiaminoxanthydrol; this changes into pyronin at once in acid solution, and a similar behaviour on the part of the cyano-compound would have proved the salt-forming rôle of the oxygen atom.

A great difference between the slightly basic tetramethyldiaminoxanthone and the non-basic dicyano-compound was found, however, in their behaviour towards oxalyl chloride. Whereas the latter was remarkably resistant to this agent, and yielded only an insoluble, non-basic yellow substance, obviously the impure 9 : 9-dichloroxanthen, the former reacted even in very dilute benzene

solutions to form a magenta-like salt, m. p. 226°, which dissolved in water and could only be regarded as 9-*chloropyronin* (annexed formula), such a rearrangement of the original keto-chloride being exemplified also in the action of oxalyl chloride on Michler's ketone (Staudinger, A., 1909, i, 905). Half the chlorine can be precipitated in cold solutions, but, on warming, the original xanthone is reproduced. The compound also condenses readily with tertiary aromatic bases in chloroform solution, giving new dyes which belong to both the pyronin and the triphenylmethane series.



J. C. W.

The Colour Reaction of Adrenaline with Dichromates. AKIRA OGATA (*J. Pharm. Chim.*, 1916, [vii], **14**, 144—145; from *Yakugakuzasshi*, 1916, **411**).—The author has examined the brown precipitate formed by the action of dichromates on adrenaline, and considers that it is chromium dioxide, CrO_2. He considers that the brown precipitate, obtained by the addition of a dichromate solution to an alcoholic maceration of the medullary substance of the suprarenal capsules, has the same composition. He has been unable to extract any colouring matter from the precipitate. The reduction of the dichromate is caused by the two phenolic groups in the ortho-position of the adrenaline nucleus.

W. G.

The Morphine Alkaloids. III. J. VON BRAUN (*Ber.*, 1916, **49**, 977—989. Compare A., 1914, i, 1138; this vol., i, 500).—The application of cyanogen bromide as a reagent in the investigation of morphine alkaloids has now led to the preparation of derivatives of morphine and codeine in which the usual methyl radicles attached to nitrogen or oxygen, as the case may be, are replaced by other alkyl groups. These compounds have been examined for two reasons: first, on account of their physiological interest, and secondly, in order to find whether any particular alkyl radicle attached to nitrogen would so weaken the molecule that the nitrogen ring would be ruptured under the influence of cyanogen bromide. Of a large number of such compounds, only two were found to have any unusual physiological effect, namely, those in which the allyl group was attached to nitrogen. These are quite antagonistic to morphine, and such a discovery invites to similar investigations with other alkaloids. With regard to the rupture of the nitrogen ring, the experience is that there is no more stable nitrogen ring system known than that of morphine. Only when the chain attached to the nitrogen atom numbers five carbon atoms is the molecule so weakened that rupture of the ring becomes the prominent effect of the treatment with cyanogen bromide.

The preparation of ethers from cyanonormorphine is easy if the alkyl haloid is highly reactive, but usually some of the compound is decomposed by the sodium ethoxide. To avoid this, the *sodium*

compound of cyanonormorphine was prepared, but it proved to be a very stable, indifferent substance. The subsequent hydrolysis of the cyano-group, however, is easy (compare the *iso*amyl derivatives, *loc. cit.*). *Cyanonorcodethyline*, $OEt\cdot C_{16}H_{14}O(OH)\colon N\cdot CN$, has m. p. 225—226°, and *norcodethyline* has m. p. 156°, and forms a *hydrochloride*, slender needles with $2H_2O$, m. p. 295° (anhydrous), a *platinichloride*, m. p. 229°, and a *nitroso*-compound, yellow needles, m. p. 205°. $\alpha\epsilon$-Di-iodopentane reacts very easily with cyanonormorphine or morphine in the presence of alcoholic alkali hydroxide. The *compound*, $[CN\cdot N\colon C_{16}H_{14}O(OH)\cdot O\cdot]_2C_5H_{10}$, has m. p. 226—230°, whilst the *pentamethylenedinormorphine* obtained from it on hydrolysis has m. p. 132—133°, forms a *hydrochloride*, m. p. 235—240°, a *platinichloride*, m. p. 250°, and a *dinitroso*-compound, m. p. 145—150, and may be reduced to the *dihydrazine*, $[NH_2\cdot N\colon C_{16}H_{14}O(OH)\cdot O]_2C_5H_{10}$, m. p. 140—145°. The corresponding *pentamethylenedimorphine* does not crystallise readily. Allyl iodide reacts still more rapidly, forming *cyanonorcodallyline* (*cyanoallylnormorphine*), m. p. 221°, which yields *norcodallyline* (O-*allylnormorphine*) on hydrolysis, mixed, however, with a considerable proportion of a phenolic substance, which is being investigated further. The normal product has m. p. 164°, and forms a *hydrochloride*, needles with $1H_2O$, m. p. 240°, a *platinichloride*, $1H_2O$, which sinters above 250°, and a *nitroso*-compound, m. p. 176°.

The *N*-alkyl derivatives of norcodeine are easily prepared (compare the phenylethyl derivative, *loc. cit.*). Those with an even number of carbon atoms in the alkyl group crystallise well; the others are usually viscous oils. N-*Ethylnorcodeine*,

$$OMe\cdot C_{16}H_{14}O(OH)\colon NEt,$$

has m. p. 103°; the *propyl* derivative forms a *hydrochloride*, m. p. 185°, and a *platinichloride*, m. p. 216°; the n-*butyl* derivative has m. p. 100°, and forms a hydrochloride and a *platinichloride*, $3H_2O$, m. p. 205°; the iso*amyl* derivative yields a *picrate*, m. p. 100°, and a *platinichloride*, $3H_2O$, m. p. 207°; the *benzyl* derivative has m. p. 60°; the *allyl* derivative has m. p. 95°, forms a very hygroscopic *hydrochloride*, m. p. 125°, and a *platinichloride*, m. p. 214°, and reacts with more allyl iodide to form the *alliodide*, $C_{23}H_{28}O_3NI$, m. p. 208° (decomp.). Dihydronorcodeine also forms an *N*-allyl derivative, which yields a crystalline *alliodide*, m. p. 157°, and is also physiologically antagonistic to morphine. On reduction with hydrogen in the presence of palladium, both allyl compounds completely lose their peculiar activity, which is also the case when the nitrogen ring is disturbed. If, for example, allylnorcodeine alliodide is treated with an alkali hydroxide, it changes into the allyl derivative of the morphimethine series, which is an inactive oil and forms an *alliodide*, $C_{26}H_{32}O_3NI$, m. p. 173°, and a *platinichloride*, m. p. 78°. Norcodeine also reacts with ethylene oxide to form N-β-*hydroxyethylnorcodeine*, $OMe\cdot C_{16}H_{14}O(OH)\colon N\cdot CH_2\cdot CH_2\cdot OH$, slender needles, m. p. 197°.

The foregoing *N*-alkyl compounds may be nitrated, acetylated, or chlorinated just like codeine, but most of the derivatives are

oily. *Nitroisoamylnorcodeine*, $NO_2 \cdot C_{16}H_{13}O(OH)(OMe):N \cdot C_5H_{11}$, m. p. 90°, forms an *acetate*, m. p. 62°, which, on treatment with cyanogen bromide, yields a small amount of nitrocyanoacetylnorcodeine (*loc. cit.*) mixed with a brominated oil, which reacts with piperidine to form the *base*,

$$NO_2 \cdot C_{16}H_{12}O(OMe)(OAc) < {N(CN) \cdot C_5H_{11} \atop NC_5H_{10}}.$$

J. C. W.

Yohimbine. V. The Hofmann Degradation. Methylyohimboaic Acid. L. SPIEGEL and M. CORELL (*Ber.*, 1916, **49**, 1086—1090. Compare this vol., i, 286).—It was hoped to apply the Hofmann reaction to yohimbine methiodide or the corresponding base, but these are found to be extremely easily hydrolysed. Methylamine is liberated when the methiodide is heated with potassium hydroxide, and when it is treated with silver oxide in the light it is oxidised. Moreover, when a cold methyl-alcoholic solution is shaken with silver oxide in the dark, methylyohimboaic acid, m. p. 304°, is readily formed. It follows, therefore, that the methyl group in this acid is attached to a nitrogen atom which is free from methyl in yohimbine, and this explains why attempts to prepare yohimbine by esterifying the acid have been fruitless.

Ethyl methylyohimboate hydrochloride, $C_{23}H_{30}O_3N_2,HCl,H_2O$, was isolated as very soluble leaflets, m. p. 273°. J. C. W.

Pyrrole-Black. II. A. ANGELI and LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 761—774. Compare A., 1915, i, 991).—The authors have made a number of experiments to ascertain under what conditions pyrrole-black is obtained most easily and in best yield. In addition to pyrrole-black, the oxidation of pyrrole yields other coloured products of approximately the same composition, and brown, chestnut, and yellowish-white products have been isolated and analysed. The last of these, m. p. 164°, exhibits a marked tendency to furnish blue compounds.

The action of hydrogen peroxide in acetic acid solution on the following compounds has also been investigated: (1) 2:4-dimethylpyrrole, which yields *γ-amino-α-methylvaleric acid*,

$$NH_2 \cdot CHMe \cdot CH_2 \cdot CHMe \cdot CO_2H,$$

forming colourless crystals, m. p. 138° (gas evol.), and giving an intense blue coloration with copper sulphate in alkaline solution; (2) 2:5-dimethylpyrrole, which gives no definite product; (3) 2-methylindole, which gives the compound, m. p. 208°, obtained by oxidation of 2-methylindole with ethereal hydrogen peroxide solution (compare Plancher and Colacicchi, A., 1911, i, 566); (4) indole, which gives a compound similar to that obtained in the preceding case. T. H. P.

Preparation of 4-Hydroxypiperidine. B. EMMERT (D.R.-P., 292456; from *J. Soc. Chem. Ind.*, 1916, **35**, 868).—4-Hydroxypiperidine is obtained by the reduction of 4-hydroxypyridine with an alkali metal and alcohol, or with hydrogen in presence of a catalyst of the platinum group. G. F. M.

Compounds of Pyridine with the Alkali Metals. BRUNO EMMERT (*Ber.*, 1916, **49**, 1060—1062. Compare A., 1915, i, 454).—When the dipyridine compound of sodium is heated at 130° in a vacuum it loses one molecule of the base and changes into the *compound* C_5H_5NNa. Lithium also quickly reacts with pyridine, and likewise gives two *compounds*; potassium reacts much more sluggishly, but the same *products* may be isolated. J. C. W.

The Reaction of the Alkyl Nitrites with Pyridine and Quinoline. CHARLES WESLEY ADDY and ALEXANDER KILLEN MACBETH (T., 1916, **109**, 754—755).—A mixture of amyl nitrite and pyridine gives a dark red liquid, from which needle-shaped crystals separate in a few days. When kept in a sealed tube, a mixture of freshly distilled pyridine and amyl nitrite showed no deposit after several weeks, but on opening the tube needles appeared in a day. A mixture of pyridine and amyl nitrate similarly kept in a sealed tube gave no deposit. The above crystalline precipitate when purified did not give the nitrite reaction, and analysis showed it to be pyridine nitrate, C_5H_5N,HNO_3. Similar results were obtained by using quinoline or α- or β-picoline in place of the pyridine. W. G.

Preparation of Isatin. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 292394; from *J. Soc. Chem. Ind.*, 1916, **35**, 830).—Isatin is obtained by heating 3-amino-2:4-dihydroxyquinoline hydrochloride with ferric chloride solution, and since this substance can be prepared from anthranilic acid (D.R.-P., 102894 and 117167) the new method affords a cheap means of obtaining isatin from naphthalene. G. F. M.

Preparation of Soluble Derivatives of 2-Phenylquinoline-4-carboxylic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 292393; from *J. Soc. Chem. Ind.*, 1916, **35**, 867—868).—Salts of amino-2-phenylquinoline-4-carboxylic-ω-methylsulphurous acid are prepared by condensing amino-2-phenylquinoline-4-carboxylic acid with formaldehyde and a bisulphite. They are easily soluble in water, and possess advantages over other derivatives of 2-phenylquinoline-4-carboxylic acid for therapeutic purposes. G. F. M.

[Methylphenazonium Iodides.] F. KEHRMANN (*Ber.*, 1916, **49**, 1207—1210. Compare this vol., i, 431, etc.)—A reply to Hantzsch. A chronological summary of the controversy over the constitution of various azonium salts. J. C. W.

Some Simple Thiazole Bases. S. GABRIEL (*Ber.*, 1916, **49**, 1110—1116).—Thiazoline and penthiazoline have been synthesised by depriving the formyl derivatives of aminoethyl or aminopropyl thiols of the elements of water, and phenpenthiazole has been obtained by condensing *o*-aminobenzyl chloride with thioformamide.

β-Aminoethyl thiol hydrochloride was heated with sodium methoxide solution and methyl formate at 100°, the residual formamide, $SH{\cdot}C_2H_4{\cdot}NH{\cdot}COH$, left as an oil on evaporation of the filtrate, was then heated with phosphoric oxide and benzene, and the thiazoline was finally isolated by distillation with potassium

hydroxide. The base (compare Willstätter and Wirth, A., 1909, i, 460) forms a *picrate*, $C_3H_5NS,C_6H_3O_7N_3$, in rhombic and hexagonal tablets, m. p. 150—151°. Similarly, β-amino*iso*propylthiol hydrochloride (Mylius, this vol., i, 634) yielded 5-*methylthiazoline*, $\begin{matrix}CHMe\cdot S\\ |\\ CH_2—N\end{matrix}\!\!>\!CH$, b. p. 143—145°/760 mm., which gave a *picrate*, m. p. 124—124·5° (decomp.).

γ-*Aminopropyl thiol*, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot SH$, was isolated from the hydrochloride (1890) by means of sodium methoxide solution as a snow-white, spongy mass, m. p. 112—113°. This was formylated as above, and finally converted into *penthiazoline*,

$$CH_2<\begin{matrix}CH_2\text{--}S\\ CH_2\cdot N\end{matrix}\!\!>\!CH,$$

b. p. 174°/758 mm., which yielded an *aurichloride*, decomp. 197—199°, a *platinichloride*, and a *picrate*, m. p. 130—132°.

A crude specimen of thioformamide (Willstätter, *loc. cit.*) obtained by shaking formamide and ether with phosphorus pentasulphide for several hours, and merely removing the solvent, was mixed with α-chloro-*o*-toluidine hydrochloride, and then the syrup was gradually treated with concentrated potassium hydroxide in order to liberate the expected *phenpenthiazole* [*dihydro*-2 : 4-*benzthiazine*], $C_6H_4<\begin{matrix}CH_2\cdot S\\ N{=\!=}CH\end{matrix}$. This is a pale yellow, viscous oil, b. p. 116—118°/6 mm., and forms an *aurichloride*, a *dichromate*, a *platinichloride*, m. p. 156—157°, and a *picrate*, long, flat needles, m. p. 181·5—186°. J. C. W.

Action of Aldehydes on *o*-Aminophenyl Mercaptan. Preparation of Benzthiazolines. M. CLAASZ (*Ber.*, 1916, **49**, 1141—1147).—Hofmann (1880) obtained benzthiazoles by the condensation of *o*-aminothiophenol with acids and also with aldehydes. A simple reaction in the latter case would have yielded thiazolines, but Hofmann explained the formation of thiazoles (which is not disputed) by assuming, without proof, that half of the aldehyde is reduced to the alcohol, thus:

$$NH_2\cdot C_6H_4\cdot SH + 2MeCHO = C_6H_4<\begin{matrix}N\\ S\end{matrix}\!\!>\!CMe + EtOH + H_2O.$$

Instead of heating the components for a long time under reflux, the author has now caused condensation to take place readily by shaking together aqueous-alcoholic solutions of the hydrochloride of the base and the aldehyde, and finds that the products under these conditions are really the benzthiazolines.

2-*Phenylbenzthiazoline* crystallises in wool-like masses of slender needles, m. p. 108—109°, and is oxidised by methyl iodide at 100° to 2-phenylbenzthiazole, the mechanism of the reaction being represented thus:

$$C_6H_4<\begin{matrix}NH\\ S\end{matrix}\!\!>\!CHPh + MeI \longrightarrow C_6H_4<\begin{matrix}NH\text{--}\\ SMeI\end{matrix}\!\!>\!CHPh \xrightarrow[-CH]{-HI}$$

$$C_6H_4<\begin{matrix}N\\ S\end{matrix}\!\!>\!CPh.$$

2-o-*Hydroxyphenylbenzthiazoline* crystallises in leaflets or scales, m. p. 130°. 2-p-*Hydroxy*-m-*methoxyphenylbenzthiazoline* forms yellow flocks, m. p. 163—165° (*picrate*, m. p. 174°). 2-p-*Methoxyphenylbenzthiazoline* is a microcrystalline powder, m. p. 105°. 2-*Styrylbenzthiazoline*, $C_6H_4<\substack{NH \\ S}>CH\cdot CH:CHPh$, forms almost colourless, woolly needles, m. p. 96°, and yields a *picrate*, m. p. 194°. Condensation of the base with glyoxal yields *bisbenzthiazoline*, $C_6H_4<\substack{NH \\ S}>CH\cdot CH<\substack{NH \\ S}>C_6H_4$, as a brown powder, m. p. 283—285°. J. C. W.

The Asymmetric Nitrogen Atom. XLIX. Behaviour of Ditertiary Aromatic Bases towards Alkyl Haloids. E. WEDEKIND and WOLD. MAYER (*Ber.*, 1916, **49**, 936—941. Compare A., 1909, i, 186).—In the earlier paper on the capacity of compounds of the type $R\cdot NPh\cdot[CH_2]_x\cdot NPh\cdot R$ to combine with alkyl haloids, it was shown that aminoammonium salts or diquaternary salts are usually formed, according to the value of x and the size of the radicle R. In one case, however, it was shown that both salts could be obtained by varying the conditions under which the alkyl haloid is applied, namely, in the case of the action of allyl iodide on diphenyldimethylpropylenediamine. Such a case is of particular interest, because the aminoammonium salt, being still possessed of additive power, might be expected to combine with a different alkyl haloid and so form a compound with two different asymmetric nitrogen atoms. The present paper and the following one deal with this question.

By grinding together equimolecular proportions of carefully purified allyl iodide and diphenyldimethylpropylenediamine in the cold, *phenylmethylallyl-methylanilinopropyl-ammonium iodide*, $NPhMe\cdot[CH_2]_3\cdot NPhMeI\cdot C_3H_5$, decomp. 128°, is obtained, whilst an excess of allyl iodide (2·5 mols.) gives rise to *diphenyldimethyldiallyltrimethylenediammonium di-iodide*,

$$CH_2(CH_2\cdot NPhMeI\cdot C_3H_5)_2,$$

decomp. 117°, the latter being the less stable salt. Benzyl bromide, however, yields only the diquaternary salt, even if only one molecular proportion is applied.

Attempts were made to resolve some of the bases by means of their camphorsulphonates, but without success. *Phenylmethylethylethylanilinoethyl-ammonium* d-*camphorsulphonate* forms colourless, rectangular tablets, decomp. 150°; *diphenyldibenzyldimethyltrimethylenediammonium di*-d-*camphorsulphonate* crystallises in felted needles, decomp. 172°, and the d-*bromocamphorsulphonate* decomposes at 210°.

Diphenyldimethyldiethylethylenediammonium dibromide,

$$C_2H_4(NPhMeEtBr)_2,$$

prepared like the di-iodide (*loc. cit.*), is an unstable salt, decomp. 112°. J. C. W.

The Asymmetric Nitrogen Atom. L. Stereoisomerism of Compounds containing two Nitrogen Atoms of Unlike Asymmetry. E. WEDEKIND and TH. GOOST (*Ber.*, 1916, **49**, 942—949. Compare preceding abstract).—The existence of isomerides analogous to the tartaric acids in the case of compounds with two similarly asymmetric nitrogen atoms has only been partly proved (A., 1910, i, 834), and it was therefore thought that compounds with unlike nitrogen atoms would be more likely to yield isomerides, two inactive and four active ones being possible. Accordingly, phenylmethylallyl-methylanilinopropyl-ammonium iodide has been converted into *diphenylbenzyldimethylallyltrimethylenediammonium iodide-bromide*, $C_3H_5\cdot NPhMeI\cdot [CH_2]_3\cdot NPhMeBr\cdot C_7H_7$, which has been separated by fractional crystallisation from methyl alcohol into two inactive isomerides. The less soluble *α-modification* forms glistening scales, decomp. 143°, and yields a pale red d-*bromocamphorsulphonate*, a d-*camphorsulphonate*, a syrupy d-*tartrate*, a very unstable *di-iodide*, and a *perchlorate*, colourless leaflets, decomp. 163—164°. The *β-modification*, decomp. 128°, is much less stable, and the only other salt which could be obtained from it was the *perchlorate*, decomp. 142—149°.

The active salts were repeatedly crystallised, but no resolution could be realised. J. C. W.

Pyrimidines. LXXX. Mechanism of the Action of Bromine on 2-Thiolpyrimidines. TREAT B. JOHNSON and A. WILLARD JOYCE (*J. Amer. Chem. Soc.*, 1916, **38**, 1557—1566).—The action of bromine on 2-methyl- and 2-ethyl-thiolpyrimidines (Johnson and Joyce, A., 1915, i, 1003) has been investigated. In both cases additive compounds are formed quantitatively in carbon tetrachloride. 4:5-*Dibromo-2-methylthioldihydropyrimidine*,

$$SMe\cdot C{\lessgtr}{N{=\!=}CH \atop N\cdot CHBr}{\gtrless}CHBr,$$

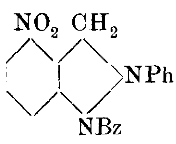
obtained at 0°, forms unstable, red needles, m. p. 65—75°. It is reconverted into 2-methylthiolpyrimidine by water, alkalis, acids, or acetone (in the last case bromoacetone is formed), and when heated under pressure at 125—135° or in carbon tetrachloride at 100° yields the *hydrobromide*, m. p. 205—206°, of 5-*bromo-2-methylthiolpyrimidine*, plates, m. p. 65—66°. The constitution of the latter was proved as follows: 5-*Bromo-2-methylthioldihydro-6-pyrimidone*, $SMe\cdot C{\lessgtr}{NH\cdot CO \atop N{-}CH}{\gtrless}CBr$, needles, m. p. 239° (decomp.), obtained by brominating 2-methylthioldihydro-6-pyrimidone in glacial acetic acid, is converted by phosphoryl chloride at 125° into 6-*chloro-5-bromo-2-methylthiolpyrimidine*, $C_5H_4N_2ClBrS$, needles, m. p. 44°, which is reduced to 5-bromo-2-methylthiolpyrimidine by zinc dust in boiling aqueous alcohol.

4:5-*Dibromo-2-ethylthioldihydropyrimidine*, which can be prepared at the ordinary temperature, is a dark-coloured oil which resembles the methyl homologue in its behaviour. 5-*Bromo-2-ethylthiolpyrimidine*, $C_6H_7N_2BrS$, needles, m. p. 43—45°, forms a *hydro-*

bromide, needles, m. p. 180° (decomp.), which is dissociated by hot water or alcohol. C. S.

Direct Nitration of Aliphatic Imino-compounds. II. Action of Absolute Nitric Acid on 3 : 5-Diketohexahydro-1 : 4-diazine-1-acetamide. J. V. DUBSKY and (FRL.) W. D. WENSINK (*Ber.*, 1916, **49**, 1041—1044).—A solution of hexamethylenetetramine and potassium cyanide was mixed with concentrated hydrochloric acid in the cold, the nitriloacetonitrile, $N(CH_2\cdot CN)_3$, which separated was hydrolysed to triglycolamic acid by means of hot hydrochloric acid, and the ester of this was converted into the amide, *nitrilotriacetamide*, $N(CH_2\cdot CO\cdot NH_2)_3$, which crystallises in large, glistening leaflets, decomp. 205—206°. This amide was then heated at 200° and the imide, 3 : 5-*diketopiperazine*-1-*acetamide*, $NH_2\cdot CO\cdot CH_2\cdot N{<}\begin{smallmatrix}CH_2\cdot CO\\ CH_2\cdot CO\end{smallmatrix}{>}NH$, was obtained in large aggregates of crystals, m. p. 215—216°, which formed a *nitrate*, glistening leaflets, decomp. 128°, with dilute nitric acid, and was oxidised by pure nitric acid to 2 : 3 : 5 : 6-*tetraketopiperazine*-1-*acetic acid*, $NH{<}\begin{smallmatrix}CO\cdot CO\\ CO\cdot CO\end{smallmatrix}{>}N\cdot CH_2\cdot CO_2H$. This crystallises in pale yellow leaflets, decomp. 230—240°, and is quantitatively hydrolysed by boiling water (or lime water) to ammonia, glycine, and oxalic acid. J. C. W.

The Oxidation of 6-Nitro-2-benzylideneaminobenzylaniline. S. REICH (*Bull. Soc. chim.*, 1916, [iv], **19**, 264—265).—6-Nitro-2-benzylideneaminobenzylaniline, when oxidised in hot acetone solution by the addition of a hot, concentrated solution of potassium permanganate, yields a *compound*, pale yellow crystals, m. p. 226°, having the composition $C_{20}H_{15}O_3N_3$, which the author regards as 4-*nitro*-1-*benzoyl*-2-*phenyldihydroindazine* (annexed formula), the oxidation causing the loss of two atoms of hydrogen and the addition of one atom of oxygen to the molecule. The compound is not acted on by weak acids. When warmed with concentrated hydrochloric acid it dissolves, and immediately after a *compound*, colourless crystals, m. p. 202° (decomp.), is precipitated. The compound, m. p. 226°, is basic in character, but does not furnish either an acetyl or a nitroso-derivative, but it is converted by phenylhydrazine into a red substance. W. G.



Quinazolines. XXXIII. New and Sensitive Indicator for Acidimetry and Alkalimetry and for the Determination of Hydrogen-Ion Concentrations between the Limits of 6 and 8 on the Sörensen Scale. MARSTON TAYLOR BOGERT and GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1916, **38**, 1606—1615).—*Dinitrobenzoylenecarbamide* [6 : ?-*dinitro*-2 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydroquinazoline*], $C_6H_2(NO_2)_2{<}\begin{smallmatrix}NH\cdot CO\\ CO-NH\end{smallmatrix}$, pale greenish-yellow prisms,

decomp. 274—275° (corr.), is obtained as follows: A solution of anthranilic acid in warm dilute hydrochloric acid is filtered, cooled, and treated slowly with an aqueous solution of potassium cyanate with efficient stirring. After twenty minutes, sodium hydroxide is added with cooling to dissolve the precipitate of *o*-carbamidobenzoic acid. The crystalline sodium salt of benzoylenecarbamide which soon separates is collected after four hours, dissolved in boiling water, and the solution acidified with acetic acid. *Benzoylenecarbamide* [2 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydroquinazoline*], $C_8H_6O_2N_2$, colourless needles, m. p. 353—354° (corr.), thus obtained in 92% yield, is converted into the dinitro-compound by concentrated nitric (D 1·42) and sulphuric acids at 100°. The *sodium* salt,

$$C_8H_3O_6N_4Na,H_2O,$$

bright yellow needles, is obtained by cooling a solution of 25 grams of dinitrobenzoylenecarbamide in 115 c.c. of *N*-NaOH and 500 c.c. of boiling water. It behaves as a very valuable indicator of hydrogen-ion concentrations between the limits 6 and 8 on the Sörensen scale; hitherto no satisfactory indicator has been known covering this range. The indicator is prepared by dissolving 0·292 gram of the salt in 100 c.c. of water. It is colourless at the limit 6 and greenish-yellow at the limit 8. It is but slightly affected by neutral salts, and not at all by chloroform or toluene. Proteins have no more influence on it than on *p*-nitrophenol. Its colour fades very slightly in a week, and is unchanged by nitrous acid. The indicator can be used in the cold or at 100°. It gives a sharp end-point with aqueous ammonia and with hydrochloric acid, but cannot be used in the titration of carbonates.

For the preparation of neutral ammonium citrate solutions for fertiliser or soil analysis it should prove superior to rosolic acid.

C. S.

Dyes of the Methylene-Blue Group. II. Phenyl Derivatives of Methylene-Blue and Thionine. F. KEHRMANN [with ADRIEN ROBERT and MAURICE SANDOZ] (*Ber.*, 1916, **49**, 1013—1023).—At Ehrlich's request the author synthesised a dye in which one methyl radicle of methylene-blue was replaced by phenyl. It was expected that this exchange would cause a change in colour towards the green, but it was found that the absorption band in the visible spectrum was displaced in just the opposite direction. The author was therefore led to examine a whole series of methyl and phenyl derivatives of thionine.

An alcoholic solution of thiodiphenylamine and methylaniline was treated with ferric chloride, and the resultant 3-*methylanilinophenazthionium* base was isolated as the dark green *ferrichloride*, and converted into the greenish-black *nitrate*, the *platinichloride*, the *bromide*, the *sulphate*, and the sparingly soluble, violet-brown *perchlorate*, of the general formula $C_6H_4{<}{\genfrac{}{}{0pt}{}{-N-}{SX}}{\gg}C_6H_3{\cdot}NPhMe$. The nitrate was treated with dimethylamine and so converted into *phenyltrimethylthionine salts*, $NMe_2{\cdot}C_6H_3{<}{\genfrac{}{}{0pt}{}{-N-}{SX}}{\gg}C_6H_3{\cdot}NPhMe$;

nitrate, metallic-green needles; *platinichloride*, greyish-blue; *iodide* and *perchlorate*, sparingly soluble. Using methylaniline instead of dimethylamine, the salts of s-*diphenyldimethylthionine* were obtained; *zincichloride*, needles with coppery lustre; *platinichloride*, a bluish-violet powder; *iodide* and *perchlorate*, dark blue precipitates. The above 3-methylanilinophenazthionium bromide yielded with aniline the *bromide* of *diphenylmethylthionine*,

$$NHPh\cdot C_6H_3{<}{\genfrac{}{}{0pt}{}{-N-}{SBr}}{\geqslant}C_6H_3\cdot NPhMe,$$

in metallic-green needles, from which the *base* was isolated in the form of brassy needles, m. p. 145°. 3-Aminophenazthionium chloride was also treated with methylaniline, and the resultant *chloride* of as-*phenylmethylthionine*,

$$NH_2\cdot C_6H_3{<}{\genfrac{}{}{0pt}{}{-N-}{SCl}}{\geqslant}C_6H_3\cdot NPhMe,$$

a bronze-like powder, was converted into the dark blue *platinichloride*.

The mono-acid salts of these and other thionines were compared spectrographically, and the results are tabulated. The chief maximum in the ultraviolet is almost exactly the same in each case, namely, at $\lambda = 290\,\mu\mu$. It will be shown later on that the position of this maximum is connected with the constitution of a dye.

J. C. W.

Hydroxy- and Methoxy-derivatives of "Thioindigo." P. FRIEDLAENDER (*Ber.*, 1916, **49**, 955—966).—Whilst hydroxyindigotins are sensitive towards alkalis (A., 1915, i, 593), it was to be expected that the "hydroxythioindigos" would not differ much from "thioindigo" [2 : 2′-bisoxythionaphthen] in this respect. Typical compounds of this class have been synthesised by well-known methods, and they are found to be quite normal dyes. The experiments were completed some years ago, and the products have since become the subjects of many patents.

o-Nitrotoluenesulphonic acid is converted into sulphoanthranilic acid by means of sodium hydroxide (D.R.-P., 138188), and this is diazotised and treated with thioglycollic acid. The 2-carboxy-5-sulphophenylthiolacetic acid,

$$SO_3H\cdot C_6H_3(CO_2H)\cdot S\cdot CH_2\cdot CO_2H,$$

so obtained forms a *barium* salt, $C_9H_4O_7S_2Ba,H_2O$, and yields a solution of the sodium salt of 3-hydroxy-6-sulphothionaphthen-2-carboxylic acid on heating with concentrated sodium hydroxide at 125°. This solution is readily oxidised by potassium ferricyanide to 2 : 2′-*bisoxythionaphthen*-6 : 6′-*disulphonic acid*, which crystallises in violet leaflets with coppery lustre and forms a *barium* salt, microscopic, red needles. The free acid obtained in glistening leaflets from the above sodium salt condenses with isatin to form the *compound* $SO_3H\cdot C_6H_3{<}{\genfrac{}{}{0pt}{}{CO}{-S-}}{>}C{:}C{<}{\genfrac{}{}{0pt}{}{-CO-}{C_6H_4}}{>}NH$, greenish-black, long, slender needles (*barium* salt), and yields 2 : 2′-*bisoxythionaphthen*-6-*sulphonic acid*, microscopic, red needles, on boiling with alcoholic dibromoketodihydrothionaphthen. The replacement of

the sulphonic acid group by hydroxyl in the above acid is effected by alkaline fusion at 180—200°. At first 5-*hydroxy*-2-*carboxyphenylthiolacetic acid* is formed, in white needles, m. p. 223° (decomp.), whilst the prolonged action results in the formation of 3:6-*dihydroxythionaphthen*, $OH\cdot C_6H_3<\overset{C(OH)}{\underset{S}{}}>CH$, in pale pink leaflets, m. p. 212—213° (*dimethyl* ether, white needles, m. p. 72—78°). This is oxidised by alkaline ferricyanide to 6 : 6′-*dihydroxy*-2 : 2′-*bisoxythionaphthen*, which separates in orange-red masses, and forms a greenish-black potassium salt and a graphite-like *barium* salt.

6:6′-Dimethoxy-2:2′-bisoxythionaphthen is obtained by methylating the above dye and also synthesised from 4-methoxyanthranilic acid, as follows: the acid is converted into 5-*methoxy*-2-*carboxyphenylthiolacetic acid*, $CO_2H\cdot C_6H_3(OMe)\cdot S\cdot CH_2\cdot CO_2H$, small, brownish-yellow needles, m. p. 218—219° (decomp.), and this into 3-*hydroxy*-6-*methoxythionaphthen*, slender, white needles, m. p. 119°, which, on oxidation, yields 6:6′-*dimethoxy*-2:2′-*bisoxythionaphthen* in red needles. The corresponding ethoxy-compounds are obtained in the same way; 4-*ethoxyanthranilic acid*, glistening leaflets, m. p. 174° (decomp.), prepared by hydrolysing the *acetyl* derivative, m. p. 182—183°, which is derived from 4-ethoxy-*o*-acetotoluidide by oxidation; 5-*ethoxy*-2-*carboxyphenylthiolacetic acid*, brownish needles, m. p. 208—209° (decomp.); 3-*hydroxy*-6-*ethoxythionaphthen*, pale red needles, m. p. 124—125° (*methyl ether*, m. p. 83°); 6:6′-diethoxy-2:2′-bisoxythionaphthen, felted, red needles, commercially known as "helindon-orange R" or "thioindigo-orange R."

5:5′-Dimethoxy-2:2′-bisoxythionaphthen is synthesised from 5-*methoxyanthranilic acid*, colourless needles, m. p. 179—180° (*hydrochloride*, m. p. 210°), which is prepared by hydrolysing the *acetyl* derivative, $CO_2H\cdot C_6H_3(OMe)\cdot NHAc$, m. p. 161—162°. The latter is obtained from two known compounds; either 5-hydroxy-*o*-acetotoluidide is converted by means of methyl sulphate into 5-*methoxy*-o-*acetotoluidide*, m. p. 134°, which is oxidised by permanganate, or 5-hydroxyanthranilic acid is converted into the *acetyl* compound, glistening leaflets, m. p. 227°, and then methylated. 4-*Methoxy*-2-*carboxyphenylthiolacetic acid*, yellow needles, m. p. 200° (decomp.), and 5:5′-*dimethoxy*-2:2′-*bisoxythionaphthen*, dark violet needles, may then be prepared as above. A poor yield of 5:5′-*dihydroxy*-2:2′-*bisoxythionaphthen*, bluish-violet flocks, is obtained by heating the latter with aluminium chloride in nitrobenzene at 160°.

4:4′-Dimethoxy-2:2′-bisoxythionaphthen is synthesised from 2-amino-6-methoxybenzonitrile. This is converted into 2-*cyano*-3-*methoxyphenylthiolacetic acid*, yellow needles, m. p. 182°, and ultimately into 4:4′-*dimethoxy*-2:2′-*bisoxythionaphthen*, which exhibits a brilliant yellow fluorescence in nitrobenzene and crystallises in pale red needles. The corresponding ethoxy-compounds are as follows: 2-*amino*-6-*ethoxybenzonitrile*, long, white needles, m. p. 98·5°; 2-*amino*-6-*ethoxybenzamide*, long needles, m. p. 169°;

2-*cyano*-3-*ethoxyphenylthiolacetic acid*, yellow needles, m. p. 172°; 4 : 4′-*diethoxy*-2 : 2′-*bisoxythionaphthen*, long, pale red needles.

With regard to the colours of these isomeric dyes, it is pointed out that corresponding hydroxy- and alkyloxy-derivatives are almost identical, but that the positions of these substituents are of great influence. The 6 : 6′-derivatives are orange-red, the 5 : 5′-isomerides are bluish-violet, whilst the 4 : 4′-compounds do not differ much in colour from "thioindigo." J. C. W.

Formamidines. V. Some Pyrazolone Derivatives. F. B. DAINS, H. R. O'BRIEN, and C. L. JOHNSON (*J. Amer. Chem. Soc.*, 1916, **38**, 1510—1517).—Dains and Brown (A., 1909, i, 781) have shown that disubstituted formamidines react smoothly with pyrazolones to form a primary amine and a substituted 4-aminomethylenepyrazolone. The following have now been prepared by heating the components at 120—150°; in some cases a bispyrazolone is also formed. 1-p-*Tolyl*-4-m-*toluidinomethylene*-3-*methyl*-5-*pyrazolone*, $C_6H_4Me\cdot NH\cdot CH{:}C<\begin{matrix}CO-N\cdot C_6H_4Me\\ CMe{:}N\end{matrix}$, golden-yellow crystals, m. p. 122°; the corresponding 4-o-*toluidinomethylene* compound, $C_{19}H_{19}ON_3$, yellow needles, m. p. 176·5°; 1-p-*tolyl*-4-o-*ethoxyanilinomethylene*-3-*methyl*-5-*pyrazolone*, canary-yellow needles, m. p. 133°; 1-p-*tolyl*-4-p-*bromoanilinomethylene*-3-*methyl*-5-*pyrazolone*, yellow crystals, m. p. 196—197°; and *methenylbis*-1-p-*tolyl*-3-*methyl*-5-*pyrazolone*, $C_{23}H_{22}O_2N_4$, orange needles, m. p. 249°. The last-named substance is formed by heating together di-*m*-tolylformamidine and 1-*p*-tolyl-3-methyl-5-pyrazolone; in a similar manner di-*p*-chlorophenylformamidine and 1-*o*-tolyl-3-methyl-5-pyrazolone yield *p*-chloroaniline and *methenylbis*-1-o-*tolyl*-3-*methyl*-5-*pyrazolone*, $C_{23}H_{22}O_2N_4$, orange needles, m. p. 190°, the same product also being formed when orthoformic ester is used instead of the formamidine. A third method of obtaining the bispyrazolones is by heating an anilinomethylenepyrazolone with a pyrazolone unsubstituted in position 4.

In the following cases a cleaner product is secured by heating the disubstituted formamidine and the pyrazolone in a solvent of high b. p., such as xylene: 1-o-*tolyl*-4-*anilinomethylene*-3-*methyl*-5-*pyrazolone*, reddish-brown crystals, m. p. 140°; 1-o-*tolyl*-4-m-*xylidinomethylene*-3-*methyl*-5-*pyrazolone*, yellow needles, m. p. 232°; and 1-o-*tolyl*-4-o-*ethoxyanilinomethylene* - 3 - *methyl* - 5 - *pyrazolone*, yellow crystals, m. p. 160°.

3-Phenyl-1-*o*-tolyl-5-pyrazolone reacts easily with disubstituted formamidines; 3-*phenyl*-1-o-*tolyl*-4-*anilinomethylene*-5-*pyrazolone*, light yellow needles, m. p. 169°, the corresponding 4-m-*xylidinomethylene* compound, yellow crystals, m. p. 142°, and the 4-p-*chloroanilinomethylene* compound, yellow crystals, m. p. 181°.

1-*Phenyl*-4-o-*ethoxyanilinomethylene*-3-*methyl*-5-*pyrazolone*, yellow needles, m. p. 170°, and the corresponding 4-m-*xylidinomethylene* derivative, golden-yellow needles, m. p. 173°, have been prepared from 1-phenyl-3-methyl-5-pyrazolone and the requisite formamidine on the water-bath.

Not only substances containing a methylene group, but also in some cases their condensation products with aldehydes, react with formamidines; thus 1-phenyl-4-benzylidene-3-methyl-5-pyrazolone, when heated with diphenylformamidine, yields benzylideneaniline and 1-phenyl-5-anilinomethylene-3-methyl-5-pyrazolone.

By treatment with hydrogen chloride in benzene, these aminomethylenepyrazolones yield additive compounds. Thus, 1-phenyl-4-*m*-xylidinomethylene-3-methyl-5-pyrazolone forms a colourless *hydrochloride*, $C_{19}H_{19}ON_3,HCl$, m. p. 189—190°. 1-Phenyl-4-anilinomethylene-3-methyl-5-pyrazolone similarly yields a *hydrochloride*, m. p. 186° (decomp.), but when boiled with alcoholic hydrogen chloride is converted into aniline and methenylbis-1-phenyl-3-methyl-5-pyrazolone. Similar results were obtained by hydrolysis with alkali; by heating with alcoholic potassium hydroxide, 3-phenyl-1-*o*-tolyl-4-anilinomethylene-5-pyrazolone yields aniline and *methenylbis*-3-*phenyl*-1-o-*tolyl*-5-*pyrazolone*, orange-yellow crystals, m. p. 179°.

1-*Phenyl*-4-m-*nitroanilinomethylene*-3-*methyl*-5-*pyrazolone*, yellow needles, m. p. 175°, and the corresponding p-*nitroanilinomethylene* derivative, orange-yellow needles, m. p. 170°, were prepared by the general method, but neither of them appears to be the *substance*, brownish-yellow needles, charring at 255—265°, obtained by nitrating 1-phenyl-4-anilinomethylene-3-methyl-5-pyrazolone in concentrated sulphuric acid.

The preceding aminomethylene compounds contain the group $>$C:CH·NHR. The mechanism of the reaction by which pyrazole and *iso*oxazole compounds are formed from them, and their behaviour with bromine, prove that they react also in the tautomeric form $>$CH·CH:NR. The dibromide obtained from the latter form may, under the influence of solvents, either lose its bromine entirely or undergo rearrangement, yielding a monobromo-substitution product and hydrogen bromide. Thus, 3-phenyl-1-*o*-tolyl-4-anilinomethylene-5-pyrazolone and bromine (1 mol.) in glacial acetic acid yield a *dibromide*, $C_{23}H_{19}ON_3Br_2$, yellow crystals, m. p. 238°, which is converted by alcohol into 3-*phenyl*-1-o-*tolyl*-4-p-*bromoanilinomethylene*-5-*pyrazolone*, blunt, yellow needles, m. p. 143°; the latter is formed from di-*p*-bromophenylformamidine and the phenyl-o-tolylpyrazolone by the general method. 3-*Phenyl*-1-o-*tolyl*-4-m-*bromoanilinomethylene*-5-*pyrazolone*, m. p. 148—150°, forms yellow crystals. The *dibromide*, $C_{19}H_{19}O_2N_3Br_2$, m. p. 203°, obtained from 1-phenyl-4-*o*-ethoxyanilinomethylene-3-methyl-5-pyrazolone, is converted by crystallisation from alcohol into methenylbis-1-phenyl-3-methyl-5-pyrazolone. In a similar manner the *dibromide*, m. p. 238°, of 3-phenyl-1-*o*-tolyl-4-anilinomethylene-5-pyrazolone yielded methenylbis-3-phenyl-1-*o*-tolyl-5-pyrazolone.

3-*Phenyl*-1-p-*bromophenyl*-5-*pyrazolone*, $C_{15}H_{11}ON_2Br$, colourless needles, m. p. 154—155°, prepared from *p*-bromophenylhydrazine and ethyl benzoylacetate in warm alcohol, shows the same general reactions as do other pyrazolones containing a free methylene group. Thus it forms with benzaldehyde at 120° a scarlet 4-*benzylidene* derivative, $C_{22}H_{15}ON_3Br$, not molten at 265°, with diphenylform-

amidine in kerosene at 125° aniline and 3-*phenyl*-1-p-*bromophenyl*-4-*anilinomethylene*-5-*pyrazolone*, $C_{22}H_{16}ON_3Br$, yellow needles, m. p. 188°, and with orthoformic ester *methenylbis*-3-*phenyl*-1-p-*bromophenyl*-5-*pyrazolone*, $C_{31}H_{20}O_2N_4Br_2$, reddish-yellow needles, not molten at 265°.

Ethyl benzoylacetate and di-*o*-phenetidylformamidine heated together on the water-bath yield o-*ethoxyanilinomethylenebenzoylacet*-o-*ethoxyanilide*, $OEt\cdot C_6H_4\cdot NH\cdot CO\cdot CBz\colon CH\cdot NH\cdot C_6H_4\cdot OEt$, colourless crystals, m. p. 173°, which is converted by phenylhydrazine at 120° into *o*-phenetidine and 1:5-*diphenylpyrazole*-4-*carboxy*-o-*ethoxyanilide*, $OEt\cdot C_6H_4\cdot NH\cdot CO\cdot C\mathord{<}{\scriptsize\begin{matrix}CH{=}N\\ CPh\cdot NPh\end{matrix}}$, slender needles, m. p. 118°.

The following new compounds have been prepared in the course of the investigation: ethyl malonate and di-*o*-phenetidylformamidine on the water-bath yield *ethyl* o-*ethoxyanilinomethylenemalonate*, $OEt\cdot C_6H_4\cdot NH\cdot CH\colon C(CO_2Et)_2$, long needles, m. p. 66—67°. By bromination in glacial acetic acid 1-*o*-tolyl-3-methyl-5-pyrazolone yields the 4-*bromo*-derivative, $C_{11}H_{11}ON_2Br$, yellow crystals, m. p. 116°, and 3-phenyl-1-*o*-tolyl-5-pyrazolone the 4-*bromo*-derivative, $C_{16}H_{13}ON_2Br$, brownish-yellow needles, m. p. 110°.

C. S.

Vicine and Divicine. P. A. LEVENE and JAMES K. SENIOR (*J. Biol. Chem.*, 1916, **25**, 607—622. Compare Levene, A., 1914, i, 1004, and E. Fischer, A., 1915, i, 451).—The present investigation furnishes direct chemical evidence regarding the location of the two amino-groups in divicine. The presence of an amino-group in position 2 is proved by the preparation of guanidine by oxidation of divicine sulphate with potassium chlorate and hydrochloric acid, a method which Fischer employed for the establishment of the constitution of 2-aminouric acid (*Ber.*, 1897, **30**, 571). Controls were carried out with the sulphates of synthetic 4:5-diaminotetrahydropyrimid-2:6-dione and 2:5-diaminotetrahydropyrimid-4:6-dione, the latter of which alone yielded guanidine.

The position of the amino-groups has also been determined by the comparison of the amino-ψ-uric acids prepared by the action of boiling potassium cyanate on divicine and the synthetic 2:5- and 4:5-diamino-compounds respectively. The products obtained from the former two compounds are identical with the 2-amino-ψ-uric acid described by Traube (*Ber.*, 1893, **26**, 2558), and differ materially from that obtained from the latter. 4-*Amino*-ψ-*uric acid*, $NH\mathord{<}{\scriptsize\begin{matrix}CO\text{————}NH\\ CO\cdot C(NH\cdot CO\cdot NH_2)\end{matrix}}\mathord{>}C\cdot NH_2$, crystallises from hot water in oblong plates with $1H_2O$, which it loses in forty hours at 135° in a vacuum over sulphuric acid. On treatment with hydrochloric acid in a sealed tube at 120°, it is converted into uric acid.

In confirmation of Fischer (*loc. cit.*), the authors find that on fusion with carbamide the 4:5-diamino-compound yields uric acid, whereas divicine and the 2:5-diamino-compound do not do so. The

identity of divicine with the 2:5-diaminotetrahydropyrimid-4:6-dione seems therefore to be established.

The constitutional formula for vicine already put forward (Levene, *loc. cit.*) has been confirmed by the determination of the molecular weight by the boiling-point method, using water as solvent. The figures obtained indicate the presence of a mono-nucleoside. H. W. B.

Constitution of Azoxy-compounds. A. ANGELI (*Gazzetta*, 1916, **46**, ii, 67—118).—A summary of the work published, in conjunction with Alessandri, Valori, and Ajazzi-Mancini, in a number of papers in the years 1908–1915. T. H. P.

The Relation between the Chemical Constitution and Colour of Azo-compounds. ANUKUL CHANDRA SIRCAR (T., 1916, **109**, 757—776. Compare A., 1912, i, 1037).—In order to test the validity of certain points in the theory of the colour and constitution of azo-compounds, certain new azo-compounds have been prepared, and the colours yielded by them as dyes and their absorption spectra compared with those of similar known compounds.

When 4-nitro-α-naphthylamine is diazotised in concentrated hydrochloric acid solution and added to a cold dilute alkaline solution of phenol, 4-*nitronaphthalene*-1-*azophenol*,

$$NO_2{\cdot}C_{10}H_6{\cdot}N_2{\cdot}C_6H_4{\cdot}OH,$$

pale red needles, m. p. 182—183°, is obtained. It dissolves in a boiling solution of alkali hydroxide with a deep red, and in concentrated sulphuric acid with a magenta colour, and dyes wool bright yellow. 4-*Nitronaphthalene*-1-*azosalicylic acid*, yellowish-red needles, softening at 199—200°, m. p. 222—223°, is similarly prepared. It dissolves in boiling alkali hydroxide solution with a deep red, and in concentrated sulphuric acid with a violet colour. It dyes both unmordanted and chrome-mordanted wool orange-yellow.

p-*Sulphobenzene*-1-*azo*-1′:2′:3′:4′-*tetrahydro*-4-*naphthol*, orange needles, is prepared from its sodium salt (compare Bamberger and Bordt, A., 1890, 508) by the addition of concentrated hydrochloric acid to its aqueous solution. It dissolves in alkali hydroxide with an orange-red, and in concentrated sulphuric acid with a red colour and dyes in full yellow shades.

p-*Nitrobenzene*-1-*azo*-1′:2′:3′:4′-*tetrahydro*-4-*naphthol*, orange prisms, m. p. 217°, is obtained by diazotising *p*-nitroaniline and combining it with an alkaline solution of 1′:2′:3′:4′-tetrahydro-α-naphthol. It dissolves in alkali hydroxide solution with an orange-red, and in concentrated sulphuric acid with a red colour, and dyes wool in full yellow shades. p-*Bromobenzene*-1-*azo*-1′:2′:3′:4′-*tetrahydro*-4-*naphthol*, orange-yellow needles, m. p. 147—148·5°, similarly prepared, gives similar colours in solution. It dyes wool yellow.

Benzene-1-*azo*-4-*anthrol*, violet-red, shining needles, m. p.

234—235° (decomp.) is prepared by diazotising aniline and adding it to an alcoholic solution of α-anthrol. It dissolves in alcoholic potassium hydroxide with a reddish-violet, and in concentrated sulphuric acid with a violet-black colour, and dyes wool reddish-violet. p-*Bromobenzene*-1-*azo*-4-*anthrol*, dark reddish-violet, microscopic needles, m. p. 248—249°, is obtained in a similar manner, it dissolves in alcoholic potassium hydroxide with a violet, and in concentrated sulphuric acid with a bluish-black colour, and dyes wool reddish-violet. p-*Nitrobenzene*-1-*azo*-4-*anthrol*, a dark red powder, m. p. 285°, similarly prepared, dissolves in alcoholic potassium hydroxide with a greenish-blue, and in concentrated sulphuric acid with a bluish-black colour; it dyes wool reddish-violet. p-*Sulphobenzene*-1-*azo*-4-*anthrol*, a dark red powder, prepared by adding a diazotised solution of sulphanilic acid to a solution of α-anthrol in excess of alkali hydroxide, dissolves in alcoholic potassium hydroxide with a violet, and in concentrated sulphuric acid with a bluish-black colour, and it dyes wool bright violet.

A comparison of the colour of the dyeings obtained on wool with the various azotetrahydronaphthols, azo-α-anthrols, azoanthranols, and the corresponding azophenols and azo-α-naphthols, shows that in an azo-compound the longer the chain of alternate double and single bonds in the part of the molecule containing the auxochrome, going from the auxochrome to the azo-linking by the longest possible route, the deeper is the colour, and vice versâ. Similarly, an examination of the absorption spectra shows that, in an azo-compound, the longer is this chain, the further is the head of the absorption band shifted towards the red end of the spectrum, and vice versâ. The absorption curves of the potassium salts of azotetrahydronaphthols and azoanthranols, as measured in alcoholic solution, are found to be much like the absorption curves of the potassium salts of the corresponding azo-α-naphthols and azo-α-anthrols respectively. These facts seem to support Hantzsch's views (compare A., 1900, i, 122) that the salts of *p*-hydroxyazo-compounds are true derivatives of hydroxyazobenzene, and seem opposed to the theory of Hewitt and Mitchell (compare T., 1906, **89**, 18; 1907, **91**, 1251) as to the transformation of the nitroazo-structure into the *iso*nitro-*iso*azo-form (with a diquinonoid structure) when *p*-nitrohydroxyazo-compounds are dissolved in alkali. The difference in the lengths of the chain of alternate double and single bonds in the nuclei containing the auxochrome being the primary cause of the difference of colour of any two azo-compounds, it cannot be maintained that, in order to produce azo-dyestuffs giving deeper colours than orange or brown, the auxochrome should necessarily be contained in a naphthalene nucleus. W. G.

Mechanism of the Azoimide Synthesis from Hydrazine and Nitrous Acid. F. SOMMER and H. PINCAS (*Ber.*, 1916, **49**, 1147. Compare this vol., ii, 316).—An unimportant addition to the theoretical discussion of the earlier paper. J. C. W.

Origin of the Humin formed by the Acid Hydrolysis of Proteins. II. Hydrolysis in the Presence of Carbohydrates and of Aldehydes. ROSS AIKEN GORTNER (*J. Biol. Chem.*, 1916, **26**, 177—204. Compare Gortner and Blish, A., 1915, i, 726).—The addition of carbohydrates or aldehydes to a hydrolysing mixture of a protein and hydrochloric acid produces considerable changes in the distribution of nitrogen in the hydrolysate. The humin nitrogen is usually largely increased, and is nearly all "acid insoluble." With formaldehyde, the proportion of "acid-insoluble" to "acid-soluble" humin decreases with increasing quantities of the aldehyde, although the total humin nitrogen remains constant at a figure about 150% higher than is obtained in the absence of the aldehyde.

Both tryptophan and tyrosine yield a very considerable proportion of "acid-insoluble" humin nitrogen when boiled with hydrochloric acid in the presence of benzaldehyde, and it is thought that these amino-acids constitute the source of the humin-nitrogen formed during the hydrolysis of proteins. H. W. B.

Influence of Alkali and Alkaline Earth Salts on the Rate of Solution of Caseinogen by Sodium Hydroxide. T. BRAILSFORD ROBERTSON and K. MIYAKE (*J. Biol. Chem.*, 1916, **25**, 351—361. Compare A., 1910, i, 528).—The relation between the time during which the caseinogen is in contact with the solvent and the amount of caseinogen which dissolves is expressed by the equation $x = Kt^m$, even in the presence of alkali or alkaline-earth chlorides in the sodium hydroxide solution employed as solvent. The presence of these salts decreases the rate of solution of the caseinogen, the retardation increasing with increasing concentration of the salt employed.

The product of the two constants, $K \times m$, is termed the "coefficient of penetration." Its value decreases with increasing concentration of the chlorides of sodium, potassium, calcium, strontium, or barium, between the limits of concentration employed, the acceleration of the decrease being positive in the cases of potassium and sodium chlorides, and negative in those of the other chlorides named. H. W. B.

Conjugated Sulphuric Acid of the Mucin of Pig's Stomach (Mucoitin-Sulphuric Acid). I. P. A. LEVENE and J. LÓPEZ-SUÁREZ (*J. Biol. Chem.*, 1916, **25**, 511—516. Compare A., 1913, i. 1267).—Glucosamine has been found to be one of the hydrolytic products of mucoitin-sulphuric acid. It is identified by the solubility of its hydrochloride, the character and magnitude of its optical rotation, the properties of its osazone, and conversion into chitonic acid. Mucoitin-sulphuric acid thus differs fundamentally from the conjugated sulphuric acid obtained from mucoids (chondroitin-sulphuric acid). H. W. B.

The Influence Exercised by the Degree of Reduction of the Hæmochromogens on their Spectral Properties. CH. DHÉRÉ and G. VEGEZZI (*Compt. rend.*, 1916, **163**, 209—212. Compare

ibid., 1916, **163**, 18).—Acid hæmochromogen, alkaline hæmochromogen, and ordinary alkaline hæmochromogen (formed by means of hydrazine hydrate) show, in aqueous alcoholic solutions, very different absorption spectra, according as the reduction has taken place in open or sealed tubes. The bands α and β vary in position and breadth, and the relative intensity and breadth of the bands enable several types of spectra to be distinguished. The hæmochromogens prepared in sealed tubes are products of complete reduction, whilst if the preparation takes place in open tubes, the reduction is probably incomplete. W. G.

Kephalin. IV. Phenyl- and Naphthyl-carbamidokephalin. P. A. Levene and C. J. West (*J. Biol. Chem.*, 1916, **25**, 517—519. Compare this vol., i, 298).—*Phenylcarbamidokephalin*,

$C_{41}H_{78}O_{13}NP,CNOPh$,

is prepared by the action of phenylcarbimide on kephalin in chloroform solution. The product is precipitated by acetone and purified by cooling its solution in ethyl acetate to 0°. It is obtained as a granular, amorphous powder. On reduction with hydrogen gas by Paal's method, *phenylcarbamidotetrahydrokephalin*,

$C_{41}H_{82}O_{13}NP,CNOPh$,

is formed. It is also a granular, amorphous product, but more insoluble than the mother substance.

Naphthylcarbamidokephalin, $C_{41}H_{78}O_{13}NP,CNO\cdot C_{10}H_7$, is prepared in a similar manner. It is insoluble in ethyl acetate, and is purified by solution in chloroform and reprecipitation with acetone. H. W. B.

Behaviour of Purified Proteins towards Proteolytic Enzymes. Edward M. Frankel (*J. Biol. Chem.*, 1916, **26**, 31—59).—The rate of digestion of each of thirteen proteins has been ascertained when subjected to the action of certain proteolytic enzymes.

Pepsin-hydrochloric acid liberates about 20% of the total amino-nitrogen of a protein in less than one hundred hours. Trypsin causes a cleavage of about 50% of the amino-nitrogen, but when it acts on proteins already partly digested with pepsin, about 70% of the amino-nitrogen is liberated in the same time. Erepsin, following the action of pepsin, liberates about 85% of the amino-nitrogen, whilst the successive action of pepsin, trypsin, and erepsin results in the cleavage of 85—90% of the total amino-nitrogen in the protein. H. W. B.

Reactions of Peroxydase Purified by Ultrafiltration. A. Bach (*Arch. Sci. phys. nat.*, 1916, [iv], **42**, 56—61).—Whilst phenol, guaiacol, quinol, and pyrogallol were found to give the same colour reactions with an extract of horse-radish and the same extract subjected to ultrafiltration, in presence of hydrogen peroxide, very different results were obtained with orcinol, aniline, dimethyl- and diethyl-aniline, benzidine, and *p*-phenylenediamine.

When *o*-cresol and saligenin are treated with a mixture of purified peroxydase and hydrogen peroxide, a yellow colour is produced in both cases, which changes to brown and then to reddish-brown.

Salicylaldehyde only reacts when the solution is made slightly alkaline with hydrogen dipotassium phosphate. Salicylic acid gives no reaction.

In the oxidation of *o*-cresol and saligenin, formic acid is produced, but no appreciable amount of carbon dioxide could be detected.

Ethyl alcohol is not attacked. It is considered more probable that ethyl alcohol is oxidised by a mixture than by a specific "alcoholoxydase." N. H. J. M.

A New Heterogeneous Ring, containing Arsenic in the Nucleus. Methylarsepedine (Methyl*cyclo*pentamethylenearsine). ENRIQUE V. ZAPPI (*Bull. Soc. chim.*, 1916, [iv], **19**, 290—300. Compare Gruttner and Wiernik, this vol., i, 92).—A more detailed account of work already published (this vol., i, 575), certain new derivatives being described. The author proposes the names arsedine and arsepedine for the arsenic analogues of pyridine and piperidine respectively, methyl*cyclo*pentamethylenearsine thus becoming 1-methylarsepedine. This compound has D^{18} 1·218; b. p. 156°/760 mm., 76°/36 mm., or 65°/20—22 mm., and it is volatile in steam. It has a feeble reducing action, and only very energetic reducing agents have any action on it, liberating arsenic. It does not yield its arsenic to cold or boiling nitric acid (D 1·42). In aqueous suspension it forms additive compounds with the halogens, three of which were prepared, namely, 1:1-*dichloro*-1-*methylarsepedine*, $CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>AsMeCl_2$, obtained as a very hygroscopic, viscous mass, decomposing in a vacuum giving methyl chloride and αε-dichloropentane; 1:1-*dibromo*-1-*methylarsepedine*, very hygroscopic crystals, which decompose on heating, giving methyl bromide and 1-*bromoarsepedine*, a red oil; 1:1-*di-iodo*-1-*methylarsepedine*, a yellow powder, m. p. 120° (decomp.).

1-Methylarsepedine gives a *platinichloride*, a pale yellow powder, m. p. 163°. The methiodide (*loc. cit.*) in aqueous solution on the addition of a solution of picric acid gives 1:1-*dimethylarsepedine picrate*, yellow needles, m. p. 258°. W. G.

Preparation of Organo-metallic Compounds. W. SCHLENK (D.R.-P., 292310; from *J. Soc. Chem. Ind.*, 1916, **35**, 867).—Organo-metallic compounds are obtained by treatment of substances, containing a C⁚C, C⁚N, or N⁚N linking, in suspension or solution in an indifferent medium, with a finely divided alkali metal in the absence of oxygen, moisture, or carbon dioxide. Thus stilbene is converted into disodiodiphenylethane, benzylideneaniline into disodiodianilinodiphenylethane, and azomethane into disodiohydrazomethane. On treatment with water, the alkali metal is replaced by hydrogen, whilst carbon dioxide is absorbed with formation of the corresponding carboxylic acid. G. F. M.

[Preparation of Mercurated Alcohols of the Aromatic Series.] V. GRIGNARD (*Bull. Soc. chim.*, 1916, [iv], **19**, 281).—A claim that the work described in a paper published by Abelmann (compare A.,

1915, i, 470) and more recently by the author in their joint names (compare this vol., i, 228) is really joint work; as such it was communicated to a congress at Havre in 1914. W. G.

Organic Lead Compounds. I. Mixed Lead Tetra-alkyls of the Type $R^1_3PbR^2$. GERHARD GRÜTTNER and ERIC KRAUSE. (*Ber.*, 1916, **49**, 1125—1133).—Some compounds of the above type have been prepared by the action of an excess of a magnesium alkyl haloid on lead trialkyl haloids. The latter compounds are not easily obtained; the reduction of ketones at lead cathodes has been the most recent method for preparing small quantities (compare A., 1911, i, 187, 188). It is now found that they can be readily prepared, however, by adding a solution of the halogen in carbon tetrachloride to a solution of a lead tetra-alkyl at $-75°$. Still, there is no very good method for preparing the tetra-alkyls. The addition of lead haloids to magnesium alkyl haloids (Pfeiffer, A., 1904, i, 544) is usually complicated by the formation of unsaturated lead alkyls, which distil with the tetra-alkyls and render these otherwise stable compounds very unstable. The lead trialkyl haloids must also be quite free from lead haloids. For this reason the stable chlorides or the freshly prepared bromides are quite useful, but never the iodides.

The mixed lead tetra-alkyls, like the simple ones, are mobile, volatile, poisonous liquids, with faint, raspberry-like odours. They react with halogens to form compounds of the type $PbR^1_2R^2X$, which will lead ultimately, it is hoped, to the preparation of alkyl compounds of asymmetric lead. Lead methyltriethyl differs from the others, however, in that halogens remove the methyl and not one of the three ethyl groups.

Lead trimethylethyl, $PbMe_3Et$, from magnesium ethyl bromide and trimethyl lead chloride, has b.p. 128—130°/751 mm. (corr.), $D_4^{20 \cdot 2}$ 1·8893, n_D^{19} 1·5132, $n_F - n_C^{19}$ 0·01936; *lead trimethyl*-n-*propyl* has b. p. 151—152°(corr.)/755 mm., D_4^{23} 1·7595, n_D^{21} 1·5082, $n_F - n_C^{21}$ 0·01805; *lead trimethyl*-n-*butyl* has b. p. 64·5°/14 mm, D_4^{21} 1·6740, $n_D^{22 \cdot 5}$1·5035, $n_F - n_C^{22 \cdot 5}$ 0·01705; *lead trimethyl*iso*butyl* has b. p. 165—166°(corr.)/769 mm., $D_4^{23 \cdot 5}$ 1·6684, $n_D^{21 \cdot 2}$ 1·5021, $n_F - n_C^{21 \cdot 2}$ 0·01675; *lead trimethyl*iso*amyl* has b. p. 70°/13 mm., $D_4^{21 \cdot 4}$ 1·5241, $n_D^{20 \cdot 3}$ 1·4926, $n_F - n_C^{20 \cdot 3}$ 0·01553; *lead methyltriethyl* has b. p. 70—70·5°/16 mm., $D_4^{23 \cdot 2}$ 1·7124, $n_D^{21 \cdot 3}$ 1·5158, $n_F - n_C^{21 \cdot 3}$ 0·01826; *lead triethyl*-n-*propyl* has b. p. 99·5°/16 mm., $D_4^{22 \cdot 5}$ 1·5948, $n_D^{19 \cdot 7}$ 1·5175, $n_F - n_C^{19 \cdot 7}$ 0·01719; *lead triethyl*iso*butyl* has b. p. 108·2°/16 mm., $D_4^{22 \cdot 6}$ 1·5302, $n_D^{21 \cdot 5}$ 1·5120, $n_F - n_C^{21 \cdot 5}$ 0·01686; *lead triethyl*iso*amyl* has b. p. 114·5°/13 mm., $D_4^{21 \cdot 8}$ 1·5055, n_D^{21} 1·5118, $n_F - n_C^{21}$ 0·01680. J. C. W.

Physiological Chemistry.

Rôle of Psychic and Sensory Stimuli in the Hyperglycæmia Produced by Lowering the Environmental Temperature of Dogs. B. KRAMER and H. W. COFFIN (*J. Biol. Chem.*, 1916, **25**, 423—430).—The percentage of dextrose in the blood of a dog does not vary when the animal is exposed to changes in external temperature for brief periods of three or four hours' duration, provided the animal is kept quiet. If excited, however, or rendered uncomfortable, a slight rise occurs in the dextrose content of the blood. Exposure of the animal to a low external temperature for a period of twenty-four hours or longer produces a definite hyperglycæmia. H. W. B.

Effect of Surgical Procedures on Blood-sugar and Renal Permeability. ALBERT A. EPSTEIN, JOSEPH REISS, and JACOB BRANOWER (*J. Biol. Chem.*, 1916, **26**, 25—29).—The activity of the kidney has been tested by means of the injection of phenolsulphonephthalein before and after certain surgical operations. It is found that operative procedures under anæsthesia accompanied by hyperglycæmia are associated with a reduction or impairment of renal function. From this the authors draw the conclusion that the infrequent elimination of sugar in the urine after operations is due to a diminished permeability of the kidneys. H. W. B.

Carbohydrate Metabolism. XI. Rôle of Calcium in the Regulation of the Sugar Content of the Blood. FRANK P UNDERHILL (*J. Biol. Chem.*, 1916, **25**, 447—461).—Calcium salts appear to assist in the regulation of the sugar content of the blood because (1) although their injection into normal rabbits fails to affect normal carbohydrate metabolism, a similar injection in conjunction with adrenaline produces a notable increase in the eliminated dextrose over and above that produced by the injection of adrenaline alone, and (2) the withdrawal of calcium by the introduction of sodium phosphate or oxalate intravenously or subcutaneously into normal rabbits leads to hypoglycæmia. H. W. B.

Carbohydrate Metabolism. XII. Influence of Sodium Carbonate on the Sugar Content of the Blood and on Adrenaline Hyperglycæmia and Glycosuria. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1916, **25**, 463—469. Compare preceding abstract).—The intravenous injection of sodium carbonate into rabbits induces a marked, although transient, fall in the sugar content of the blood (compare Pavy and Godden, A., 1912, ii, 68). The hyperglycæmia and glycosuria provoked by adrenaline are both significantly decreased if sodium carbonate is administered at suitable periods of time prior to the introduction of the adrenaline.

H. W. B.

Carbohydrate Metabolism. XIII. Influence of Magnesium Salts on the Sugar Content of the Blood and on Adrenaline Hyperglycæmia and Glycosuria. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1916, **25**, 471—478. Compare preceding abstracts).—Small doses of magnesium lactate introduced subcutaneously into rabbits fail to produce significant changes in the sugar content of the blood. The subsequent administration of adrenaline is accompanied by a greater hyperglycæmia and glycosuria than occurs when adrenaline alone is administered to the normal animal.

The effect on the blood and urine of the administration of magnesium sulphate to rabbits is apparently dependent on the same factors as those which control the resulting anæsthesia. If general anæsthesia develops, hyperglycæmia and glycosuria set in. If, however, the anæsthesia is absent, glycosuria is also absent, and the hyperglycæmia, if present, is not pronounced and of short duration. The injection of calcium salts during the height of magnesium anæsthesia, which quickly abolishes this state (Meltzer and Auer, A., 1908, ii, 312), also quickly restores the sugar content of blood and urine to the normal level. H. W. B.

Enzymic Actions of Blood on Dextrose. II. Destruction and Condensation of Dextrose by Blood Circulated, with or without Dextrose, in the Surviving Pancreas. UGO LOMBROSO (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 802—806. Compare this vol., i, 612).—Under normal conditions the glycolytic activity of blood is very slight, only a minimal fraction of the dextrose contained in a similar volume of the blood being destroyed. When, however, blood containing 0·5—1% of dextrose is circulated in the pancreas of a normal dog, part of the dextrose is consumed and the blood develops intense glycolytic activity capable of destroying a considerable portion of the remaining dextrose in a few hours. The tendency of the blood to condense the dextrose shows no corresponding change.

When pure blood is circulated in the pancreas of a normal dog and 0·5—1% of dextrose is added after the circulation, the glycolytic power of the blood is not modified as in the preceding case; at the most a slightly increased destruction of the dextrose occurs. Pure blood which has been circulated in the pancreas shows a marked tendency to produce in dextrose, subsequently added, the synthetic phenomenon shown in limited degree by normal blood.

T. H. P.

Enzymic Actions of Blood on Dextrose. III. Destruction and Condensation of Dextrose by Blood Circulated, with or without Dextrose, in the Surviving Intestine. UGO LOMBROSO (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 41—46).—When blood containing dextrose is circulated in the surviving intestine of a normal dog, results similar to those given with the pancreas (see preceding abstract) are obtained, except that the glycolytic enzyme exhibits still greater activity. Condensation phenomena, if occuring at all, do not surpass in extent those taking place with normal

blood. When the dextrose is added to the blood after the circulation, a distinct, although lower increase is found in the glycolytic power; in this case, however, an apparent disappearance of the dextrose, owing to condensation, is observed to a greater extent than in the experiments with the pancreas. When, under these conditions, blood is kept for a long time in the thermostat, its reducing power (1) diminishes very considerably, owing to condensation of the dextrose; (2) rises to almost exactly its initial value, owing to liberation of the dextrose; and (3) begins to decrease, in consequence of the destruction of the dextrose. These three actions are attributed to three different enzymes. T. H. P.

Distribution of the Lipoids ("Fat") in Human Blood. W. R. BLOOR (*J. Biol. Chem.*, 1916, **25**, 577—599).—The term "lipoids" is used in this paper as a general term for all those substances connected with the metabolism of the fatty acids, including the fatty acids, their naturally occurring compounds, and such substances, as cholesterol, which occur naturally in combination with the fatty acids, and are therefore presumably connected with their metabolism.

Complete analyses of the lipoids of the blood of twenty-three normal and twenty-five abnormal persons are presented, together with ratios between certain of these lipoids.

In normal blood it is found that the corpuscles contain approximately twice as much lecithin as the plasma, whilst the plasma contains almost always more cholesterol and fatty acid than the corpuscles. In the corpuscles there is twice as much lecithin as cholesterol; in the plasma the amounts are about equal. These ratios between lecithin and cholesterol are constant for normal blood and for most samples of pathological blood. The amount of fat (glycerides) in normal plasma is small; in the corpuscles it may be entirely absent.

The most characteristic feature of pathological blood is the increase of fatty acids and fat, both in plasma and corpuscles, and the decrease of lecithin in the plasma. Since the fat is probably to be regarded as the "storage" form of the body lipoids and the lecithin as the first step in its utilisation, an undue accumulation of fat or a notably decreased value for lecithin probably indicates a diminished activity of the fat metabolism.

In severe diabetes the lipoids of the blood are all greatly increased, but the ratios between the constituents are practically normal. Low values are obtained for the cholesterol of the plasma in anæmia, which confirms the view ascribing an anti-hæmolytic function to this substance. In hæmophilia, low values for lecithin (with which kephalin is included) were obtained (compare Howell, A., 1912, ii, 1078). H. W. B.

Nature of the Acid-soluble Phosphorus of Serum. ISIDOR GREENWALD (*J. Biol. Chem.*, 1916, **25**, 431—435).—The phosphorus compounds in serum consist almost exclusively of phospholipins and inorganic phosphate. There is some indication of the presence of a form which is soluble in dilute acids, but is not precipitated

by magnesia mixture or by molybdate solution, and does not dialyse readily from serum. H. W. B.

Digestibility and Utilisation of the Proteins of the Egg. W. G. BATEMAN (*J. Biol. Chem.*, 1916, **26**, 263—291).—Experiments are described in which the effects are noted of employing raw and cooked white of egg as the protein element of the diet of dogs, rats, rabbits, and men. It is found that raw white of egg is a decidedly indigestible substance. Only 50 to 70% is utilised by the body, the remainder being excreted with the fæces. When ingested in large amounts it causes diarrhœa. Of the individual proteins constituting egg-white, the albumin fraction appears to be the indigestible component. The indigestibility may be due to the anti-tryptic properties of the raw egg-white. After persistent feeding for several days a certain tolerance for the native protein is acquired, so that the symptoms described above gradually disappear.

Raw white of egg can be rendered digestible by coagulation by heat; by precipitation with alcohol, chloroform, or ether; by incubation with a dilute acid or an alkali; by partial digestion by pepsin, or by conversion into alkali metaprotein.

The white of the duck's egg behaves in the same way as that of the hen's egg in the animal body.

Egg-yolk, either raw or cooked, is excellently utilised, although it sometimes causes digestive disturbances in dogs, apparently because of its high fat content.

The extensive use of raw egg-white in current dieto-therapy is not warranted by these observations. H. W. B.

Utilisation of Inositol in the Dog. R. J. ANDERSON (*J. Biol. Chem.*, 1916, **25**, 391—397).—Inositol is not utilised to any extent by the dog. It is not stored or oxidised in the body, but as much as 77% of the amount ingested may be recovered unchanged from the excreta. It is chiefly eliminated with the fæces. H. W. B.

Utilisation of Inositol in the Animal Organism. Effect of Inositol on the Metabolism of Man. R. J. ANDERSON and A. W. BOSWORTH (*J. Biol. Chem.*, 1916, **25**, 399—407. Compare preceding abstract).—The ingestion of inositol does not have any marked effect on general metabolism in man, except the production of a slight increase in the amount of creatinine eliminated in the few days immediately following the resumption of the ordinary diet. About 9% of the ingested inositol is regained from the urine; in what manner the balance, about 91%, of the inositol is utilised has not been ascertained. The fæces remained free from inositol.
H. W. B.

Utilisation of Sucrose and the Inverting Power of the Blood Serum after Parenteral Administration of Sucrose. SHIGENOBU KURIYAMA (*J. Biol. Chem.*, 1916, **25**, 521—547).—After sucrose is administered parenterally to dogs in doses of 0·4

to 0·9 gram per kilo. of body weight, the amount which can be recovered from the urine averages 76% of the amount injected. The utilisation of the sugar is not increased after repeated injections, nor can the presence of an inverting enzyme be detected in the serum either before or after the administration of the sucrose. When solutions of yeast invertin are injected either subcutaneously or intravenously, invertase is recognisable in the serum, and sucrose subsequently injected does not reappear to such a large extent in the urine. These experiments do not support the view that the administration of sucrose to an animal leads to the protective appearance of invertase in the serum (compare Abderhalden and Grigorescu, A., 1914, i, 765). H. W. B.

Effect on Nitrogen Partition of Substituting Alcohol for Sucrose in an Otherwise Fixed Diet. FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1916, **25**, 601—605).—In two subjects accustomed to the moderate use of alcoholic beverages, the substitution in an otherwise fixed diet of alcohol for sucrose in isodynamic amounts, yielding about 370 cal., did not produce any significant changes in the nitrogen partition or in the total nitrogen excreted in the urine. H. W. B.

Mechanism of the Sparing Action of Carbohydrates on Protein Metabolism. R. A. KOCHER (*J. Biol. Chem.*. 1916, **25**, 571—576).—The author describes some experiments on fasting dogs in which, when the daily output of nitrogen in the urine had become constant, sucrose was added to the diet in some cases and equivalent quantities of lactic acid or pyruvic acid in other cases. In all cases the effect was a diminution in the urinary nitrogen, which amounted to about 60% when either sucrose or lactic acid was administered and rather less in the case of pyruvic acid.

Lactic acid therefore exerts practically the same sparing action on protein metabolism as carbohydrate, and the author considers that this constitutes evidence in favour of the view that normally lactic acid is formed as an intermediate compound in the utilisation of carbohydrates in the body, and suggests that the observed sparing action is due to the synthesis of amino-acids from lactic acid and part of the nitrogen from protein catabolism which otherwise, in the absence of suitable carbohydrate derivatives, is excreted in the urine. By means of this synthesis of amino-acids, part of the nitrogen is retained and formed into new proteins. H. W. B.

Metabolism of Sulphur. I. Relative Eliminations of Sulphur and Nitrogen in the Dog in Inanition and Subsequent Feeding. HOWARD B. LEWIS (*J. Biol. Chem.*, 1916, **26**, 61—68).—The results indicate that a retention of sulphur as compared with nitrogen does not occur during fasting. On the subsequent administration of protein, relatively more sulphur than nitrogen is at first retained by the organism, which suggests that there is a demand for replacement of sulphur compounds in the body which

meets with a prompt response. Afterwards, the nitrogen : sulphur ratio becomes less than normal, until the balance between cystine and the other amino-acids is restored. H. W. B.

Growth. V. Influence of Cholesterol on the Growth of the White Mouse. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1916, **25**, 635—646. Compare this vol., i, 350).—The administration of 40 mg. per day per animal of cholesterol to mice, beginning at five weeks after birth, leads at first to a marked retardation of growth, which is followed after the tenth week by accelerated growth, although the acceleration is insufficient to compensate entirely for the initial retardation. The animals fed on cholesterol do not differ noticeably in size from normal animals, but their coats are smoother and more glossy. H. W. B.

Growth. VI. Influence of Lecithin on the Growth of the White Mouse. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1916, **25**, 647—661. Compare preceding abstract).—The administration by the mouth of 80 mg. per day per animal of lecithin to mice does not appear to have any significant effect on growth. H. W. B.

Growth. VII. Influence of the Administration of Egg Lecithin and of Cholesterol to the Mother, on the Growth of Suckling Mice. T. BRAILSFORD ROBERTSON and ETHEL CUTLER (*J. Biol. Chem.*, 1916, **25**, 663—667. Compare preceding abstract). —The administration of 100 mg. of cholesterol per day by the mouth to the mother causes a marked retardation of the growth of suckling mice. Lecithin causes a similar retardation, though not so marked. The authors were unable to ascertain whether the retardation in growth was due to the direct action of cholesterol and lecithin on the suckling mice or only to an indirect action due to interference with the supply of milk. H. W. B.

Quantitative Comparison of Caseinogen, Lactalbumin, and Edestin for Growth or Maintenance. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1916, **26**, 1—23).—Experiments on rats are recorded which demonstrate the superior efficiency of lactalbumin in the nutrition of growth and of maintenance even when the amount of protein administered is less than that actually required for normal growth. It is found that 50% more of caseinogen or 90% more of edestin than of lactalbumin is required to produce the same gain in body-weight. The addition of cystine to caseinogen renders the latter more efficient for growth, but does not render it equal to lactalbumin. In one series of experiments where an addition of 3% of cystine was made to the caseinogen, 18% less of the protein produced $12\frac{1}{2}$% more growth as measured by increase of body-weight. H. W. B.

Feeding Experiments on the Substitution of Protein by Definite Mixtures of Isolated Amino-Acids. H. H. MITCHELL (*J. Biol. Chem.*, 1916, **26**, 231—261).—The results of these experiments with mice show that the alternate feeding of an amino acid

ration containing 4—6% of various mixtures of isolated amino-acids, together with sucrose, starch, protein-free milk, lard, and butter, and a similar ration, but free from amino-acids, induces a better total consumption of food and a longer survival period than is obtained by feeding entirely with the amino-acid ration. The absence of tryptophan from the amino-acid mixture results in a shortening of the survival period. The omission of tyrosine or of tyrosine and phenylalanine does not produce a similar effect. Possible explanations of these results are discussed. H. W. B.

Chemical Stimulation of Nerves. JACQUES LOEB and W. F. EWALD (*J. Biol. Chem.*, 1916, **25**, 377—390).—Certain phenomena connected with the chemical stimulation of nerves are described by the authors which are not in harmony with the theory of Mathews (A., 1904, ii, 627), according to which only the anions have a stimulating action and the cations a depressing action on nerves.

It is shown that a non-stimulating salt like ammonium chloride can be made a powerful nerve stimulant if for the four hydrogen atoms ethyl groups are substituted. Tetraethylammonium chloride is a more powerful stimulant for the nerve than sodium citrate. There is little difference between the stimulating power of the chloride, hydroxide, and citrate of tetraethylammonium, showing that in this case the cation, and not the anion, determines the high stimulating power. This conclusion is supported by the fact that in order to inhibit the stimulating action of the tetraethylammonium cation, through the addition of calcium chloride, the same high concentration of the latter salt is required as for the inhibition of the stimulating action of sodium citrate.

Both tetraethylammonium chloride and sodium citrate can only stimulate the nerve when the electrical irritability of the latter is at its normal height. If this irritability is only moderately diminished (by putting the nerve for two hours into an isotonic sugar solution) neither tetraethylammonium chloride nor sodium citrate will stimulate the nerve. If, however, the original irritability of the nerve is restored by bathing the latter in saline solution, tetraethylammonium chloride as well as sodium citrate will stimulate the nerve again.

When a quantity of calcium chloride is added sufficient to reduce, but not entirely to inhibit, the effect of the stimulating salts, the latent period of stimulation is considerably increased. This fact harmonises with the view of the authors that the inhibiting action of calcium is due to a prevention or retardation of the diffusion of the stimulating salt into the nerve. It is suggested that in the chemical stimulation of the nerve, potential differences are created owing to unequal diffusion occurring at different spots in the nerve. Other possible explanations of the connexion of diffusibility and stimulating action of salts are discussed. H. W. B.

Autolysis. IV. Latent Period in Autolysis. H. C. BRADLEY and JOSEPH TAYLOR (*J. Biol. Chem.*, 1916, **25**, 363—375. Compare this vol., i, 582).—The authors have investigated the cause of the

latent period occurring in the autolysis of the liver and other organs, which has been previously observed by Lane-Claypon and Schryver (A., 1904, ii, 574). It is found that the time required for the appearance of measurable amounts of amino-acids is greater than that required for the increase in non-coagulable nitrogen, and it is suggested that the latent period is due merely to the lag between the initial stages of proteolysis and the liberation of the final products.

The latent period is abolished on the addition of trypsin, a trace of acid, or even of some gelatin to the incubating tissue. After the addition of the optimum amount of acid, non-coagulable nitrogen begins to appear at once, and amino-acid nitrogen within a few minutes. Since the addition of gelatin is attended with the same result, the action of the acid is regarded as resulting in the production of an increase in the mass of tissue substratum open to the attack of the autolytic enzyme. The assumption of a progressive activation by the acid of the catalytic agent during autolysis is regarded by the authors as unnecessary. H. W. B.

Influence of Autolysis on Cholesterol Esters. J. HOWARD MUELLER (*J. Biol. Chem.*, 1916, **25**, 561—565. Compare Schultz, A., 1912, ii, 852; Cytronberg, A., 1912, ii, 1065).—Contrary to the results of previous observers (*loc. cit.*), the author finds that hydrolysis of the cholesterol esters does not occur during the autolysis of liver or blood. H. W. B.

Composition and Physiological Activity of the Pituitary Body. II. FREDERIC FENGER (*J. Biol. Chem.*, 1916, **25**, 417—422. Compare A., 1915, i, 739).—By comparison of the glands from calves with those from the mature ox, it is found that the physiological activity of the posterior lobe of the pituitary body is somewhat higher during the period of growth than after maturity has been reached. This is analogous to the conditions existing in the case of the thyroid, the thymus, and the suprarenals. The pituitary of the calf contains slightly more phosphate, both in the anterior and posterior lobes, than the corresponding gland from the ox.

The active principle of the posterior lobe of the pituitary is extracted readily from the fresh glands by water, but even more readily by acidified methyl alcohol. H. W. B.

Pituitary Gland. Its Effect on Growth and Fission of Planarian Worms. ROSALIND WULZEN (*J. Biol. Chem.*, 1916, **25**, 625—633).—The rate of fission in planarian worms is increased by a diet of pituitary substance, no matter what portion of the gland is used or what the age of the worms experimented with.

The growth of planarian worms is accelerated when the diet consists of the anterior lobe of the pituitary gland, provided the worms are very small at the beginning of the experiment. The posterior lobe does not accelerate growth. This suggests that there is a distinction between the substance which produces fission and that which produces growth. H. W. B.

Relation between the Amount of Catalase in the Different Muscles of the Body and the Amount of Work done by these Muscles. W. E. BURGE (*Amer. J. Physiol.*, 1916, **51**, 153—161).—The more work a muscle does, the more catalase does it contain. There is more catalase in the muscles of warm-blooded animals in which oxidation is intense than in the corresponding muscles of cold-blooded animals. G. B.

Thromboplastic Action of Kephalin. JAY MCLEAN (*Amer. J. Physiol.*, 1916, **46**, 250—257).—Howell's view (A., 1912, ii, 1078) that the thromboplastic substance of the tissues is akin to kephalin has at his suggestion been tested further. Kephalin was prepared from brain dried in warm air, also by Renall's (A., 1913, i, 1254) and by Levene and West's (A., 1914, i, 12) methods, and was purified as completely as possible; in all cases it was very active in causing the coagulation of a mixture of fresh serum and oxalate plasma. A kephalin-like substance could be further extracted by alcohol at 60° from cuorin, Erlandsen's phosphatide from the heart (A., 1907, i, 391), and from Baskoff's liver phosphatide (A., 1908, i, 1029). In both these cases the kephalin was active, but the purified cuorin and jecorin were inactive, as was sphingomyelin. G. B.

Composition and Morphology of Ovarian Lipoids. I. The Egg of Ascaris megalocephala. E. FAURÉ-FREMIET (*J. Physiol. Path. gén.*, 1916, **16**, 808—820).—The lipoids in the eggs of *Ascaris megalocephala* (a common worm parasitic in the intestine of cattle) amount to 21—22% of the dry weight. A peculiar constituent is the *formate* of *ascarylic acid*, crystallising from acetone or alcohol in needles melting at 39°. The acid itself forms needles melting at 82°, and probably has the composition $C_{20}H_{40}O_3$; it is a hydroxy-acid, yielding the above formate and a *monoacetyl* derivative, m. p. 50°. It is identical with ascaryl alcohol, $C_{32}H_{64}O_4$, previously described by Flury (A., 1912, ii, 464). G. B.

The Analogy in the Behaviour of Emulsions and of the Fats in the Protoplasm. MARTIN H. FISCHER and MARIAN O. HOOKER (*Kolloid Zeitsch.*, 1916, **18**, 242—262).—The fat content of the most various animal fluids and of tissue cells is very largely in excess of the quantities which may be expected to remain permanently dissolved or suspended in water, and the percentage of fat indicated by chemical tests is usually very much greater than that shown by histological methods.

The authors seek to show that the occurrence of these large quantities of fat, which are present in the cells and secretions of living organisms in a stable colloidal form, is to be attributed to the protective influence of hydrophile proteins, carbohydrates, etc. The separation of fat in such a form that its presence may be detected by the usual histological methods is supposed to correspond with the diminution in the degree of dispersity of an emulsion. Various experiments are referred to which show that fatty degeneration of tissues is not usually accompanied by any

increase in the total fat content of the cells. Under normal conditions the fat is, however, in a much more highly disperse form, and fatty degeneration consists merely in a change in the physical condition of the contained fat. The cause of this may not be evident, but the authors claim that there is a close similarity between the processes of fatty degeneration in living cells and of the coarsening of a highly disperse emulsion of oil in a hydrophile colloid.

Such an emulsion is coarsened by dilution with water or on the addition of acids, alcohol, and other substances, and it is supposed that fatty degeneration of tissues is primarily due to influences of the same kind which are brought into action indirectly by the absorption of specific substances by the organism or by various pathological conditions.

The fact that an emulsion of two liquid substances has a very much greater viscosity than either of the components affords a possible explanation of the apparently solid nature of many tissues. The softening of these under certain pathological conditions may possibly be due to a separation of the components of the emulsoid system.

Although the fat content of cell protoplasm and animal secretions is more generally to be regarded as representing the disperse phase of the colloid system, it must be remembered that increase in the concentration of the fat may lead to the formation of an emulsion of opposite type in which the fat or oil assumes the rôle of the dispersive medium. Such a transformation occurs in the preparation of butter from milk, and glandular secretions, such as ear-wax, are to be placed in this category. H. M. D.

Cell Penetration by Acids. II. Further Observations on the Blue Pigment of Chromodoris zebra. W. J. CROZIER (*J. Biol. Chem.*, 1916, **26**, 217—223. Compare A., 1914, i, 454, and this vol., i, 349).—The blue integumentary pigment of *Chromodoris zebra*, Heilprin, is found also in the blood of this nudibranch. It seems resistant towards reducing agents, but is reduced to a colourless condition by the action of putrefactive micro-organisms. In this respect the *Chromodoris* pigment resembles oxyhæmocyanin. The blue colour is regenerated on shaking with air or adding hydrogen peroxide. Only in the oxidised condition is it turned pink by acids.

It is found that protracted laboratory confinement of *Chromodoris* leads to changes in the proportion of bound to dissolved (acid-sensitive) pigment in the skin, and also to alterations in the resistance of the tissue towards acids and other agents. Unless, therefore, freshly collected specimens are employed, variations are likely to occur in the measurements of acid penetration in the case of variously pigmented *Chromodoris* tissues. H. W. B.

Cell Penetration by Acids. III. Data on some Additional Acids. W. J. CROZIER (*J. Biol. Chem.*, 1916, **26**, 225—230. Compare preceding abstract).—The penetrating ability of hexoic,

maleic, and fumaric acids has been tested for the indicator-containing tissue of the nudibranch *Chromodoris zebra*. The positions of these acids in relation to the eighteen previously studied are such as to support the conclusion derived from the latter, namely, that for any given acid at least two factors determine its relative position in the penetration series. One of these factors is degree of ionisation, and the second concerns more particularly the union of the acid with one of the several constituents of the surface of the cell. In the case of the weak monobasic fatty acids this constituent is of a fatty nature. H. W. B.

Formation of *d*-Lactic Acid by the Autolysis of Pus. HIIZU ITO (*J. Biol. Chem.*, 1916, **26**, 173—176).—*d*-Lactic acid is a constant constituent of pus. The amount of it is increased by autolysis of the pus. H. W. B.

Physiology of the Phenols. HARRY DUBIN (*J. Biol. Chem.* 1916, **26**, 69—91. Compare Folin and Denis, A., 1915, i, 1034). —The author has estimated, by the method of Folin and Denis (A., 1915, ii, 802), the daily excretion of urinary phenols by dogs under normal and pathological conditions.

The amount of phenol daily eliminated by a normal dog varies between very narrow limits. It increases when the water intake is reduced and after such operations as produce intestinal obstruction or occlusion of the bile or pancreatic ducts. In all conditions a large percentage of the phenols is excreted in an unconjugated or free form (compare Folin and Denis, *loc. cit.*). In normal cases the free phenols constitute about 75 to 85% of the total phenols. When there is a rise in the total phenols, whether due to ingested phenols or to some pathological condition, the percentage of free phenols falls to 30 to 70, although the absolute quantity excreted is increased. An increase in the formation of phenols results, therefore, in an increased conjugation, indicating a response by the protective mechanism of the body to the greater stimulus. The conjugation occurs mainly in the liver, and after Eck's fistula, which excludes the liver from the circulation, the free phenol in the urine rises to as much as 97% of the total. If, however, phenol is administered in these circumstances, increased elimination of conjugated phenols still occurs, indicating that other organs can take up the work of the liver in this respect.

Feeding with phenol, *p*-cresol, or tyrosine leads to an increased elimination, which in amount is greatest in the case of phenol. Since *p*-cresol makes up the larger part of the normal urinary phenols, it is not surprising that a greater conjugation occurs after feeding with this compound than with phenol or tyrosine. The elimination after feeding usually occurs within twenty-four hours.

Fasting reduces the urinary output of phenols to a low level. If phloridzin is now injected, a rise in the urinary phenols takes place, which may be due to the increased protein catabolism or

to the direct oxidation of the benzene nuclei contained in the injected phloridzin. H. W. B.

Uric Acid Solvent Power of Normal Urine. HOWARD D. HASKINS (*J. Biol. Chem.*, 1916, **26**, 205—215).—When shaken with uric acid at 37°, many urines that are slightly acid and all that are neutral or alkaline take up extra uric acid. The less acid the urine the more uric acid, as a rule, it will dissolve. Dilute urines show much greater solvent power than concentrated urines, even when the amounts of uric acid already present are taken into account. Some urines dissolve so much uric acid that they eventually contain more uric acid than is present in a saturated solution of sodium hydrogen urate. Apparently in these cases, at least, a part of the uric acid is present in a colloidal state. H. W. B.

The Mucilaginous Substance of Horse Urine. A. V. SAHLSTEDT (*Skand. Arch. Physiol.*, 1916, **33**, 183—216).—Normal horse urine contains a glucoprotein with the properties of a mucin and of the composition 49·5% C, 6·4% H, 12·1% N, 1·9% S, and 30·1% O. The carbohydrate complex, calculated as glucosamine, amounts to 30%. The urine also contains chondroitinsulphuric acid, and probably traces of nucleic acid. When it is acidified, all these substances give rise to an opalescence or a precipitate and show the mucin or nucleoalbumin ring with Heller's test.

In an appendix details are given of a micro-Carius method of sulphur estimation. G. B.

Excretion and Secretion of Salvarsan and Neo-Salvarsan. JOHN WEBSTER (*Analyst*, 1916, **41**, 231—237).—Salvarsan and neo-salvarsan are excreted fairly rapidly at first, the amount excreted per diem falling, as a rule, after the first day, until at the end of a week the quantity excreted is comparatively small; arsenic may, however, be found in appreciable quantity in the urine at the end of fourteen days after the dose has been given. In cases of death following the injection of either of the two substances, arsenic is found in relatively large amounts in the liver, kidneys, and spleen, and in small amounts in the muscles and blood. Arsenic is entirely, or almost entirely, absent from the brain and nervous system (compare McIntosh and Fildes, A., 1915, i, 44). W. P. S.

Nature of the Disease Due to the Exclusive Diet of Oats in Guinea-pigs and Rabbits. CASIMIR FUNK (*J. Biol. Chem.*, 1916, **25**, 409—416. Compare Morgen and Beger, A., 1915, i, 922).—The symptoms that develop in rabbits fed on oats do not disappear when lime juice, yeast extract, or other antiscorbutics are added to the diet. Since sodium hydrogen carbonate has been shown to remove the symptoms (*loc. cit.*), the disease arises probably from acidosis and does not bear any relation to scurvy. Guinea-pigs on the same diet are not influenced by the addition of alkali or

of antiscorbutics. Rats can live on oats for a considerable time, but not on oats which have been heated under pressure. Young rats fail to grow on an exclusive oat diet. H. W. B.

Influence of Ingested Carbohydrate, Protein, and Fat on the Sugar of the Blood in Phloridzin Diabetes. FRANK A. CSONKA (*J. Biol. Chem.*, 1916, **26**, 93—98).—After the administration of carbohydrate or protein to a phloridzinised dog, the rise and fall of dextrose in the blood run practically parallel to similar changes occurring in the urine. This fact indicates that in these circumstances a deposition of dextrose as glycogen does not occur between the periods of absorption and elimination. The estimation of glycogen in the liver and muscles after the experiment confirms this conclusion. H. W. B.

Physiological Action of Glucal. J. O. BALCAR (*J. Biol. Chem.*, 1916, **26**, 163—171).—The subcutaneous or intravenous injection of solutions of glucal into frogs, guinea-pigs, or dogs is not followed by any toxic symptoms. Apparently a portion of the glucal passes unchanged into the urine, and can be detected by the formation of a green precipitate on the addition of concentrated sulphuric acid. Glucal is not fermented by yeast or by *Bacillus coli*. H. W. B.

The Effect of Trinitrotoluene on Women Workers. AGNES LIVINGSTONE-LEARMOUTH and BARBARA MARTIN CUNNINGHAM (*Lancet*, 1916, **191**, ii, 261—264).—There is no constant relationship between the severity of the symptoms and the ultimate issue of the case. A worker with severe gastric derangement when taken off T.N.T. may completely recover in a short time, whereas slight loss of appetite and lassitude may (although the worker is removed from all contact with the powder) prove the gateway to serious illness and physical disaster. One fatal case is described. G. B.

Chemical Nature of the "Vitamines." I. Antineuritic Properties of the Hydroxypyridines. ROBERT R. WILLIAMS (*J. Biol. Chem.*, 1916, **25**, 437—445).—Previous investigations of the nature of the vitamines have demonstrated the presence of a pyridine derivative (compare Drummond and Funk, A., 1915, i, 112). The author has therefore prepared certain hydroxypyridines and has ascertained their curative power on polyneuritic pigeons. The series of pyridine derivatives included nicotinic, cinchomeronic, quinolinic, 6-hydroxynicotinic, and citrazinic acids, 2-hydroxypyridine, glutazine, 2:4:6-trihydroxypyridine and its anhydride, and, finally, 2:3:4-trihydroxypyridine and the so-called tetrahydroxypyridine. On treating polyneuritic pigeons with these substances, definite curative power was exerted by 2-hydroxy-, 2:4:6-trihydroxy-, and 2:3:4-trihydroxypyridine; the remaining substances did not effect any definite improvement in the condition.

Further investigation has shown that the curative action is

only obtained from freshly prepared compounds or from those compounds prepared under definite conditions which have since been, in part, determined. It is found that 2-hydroxypyridine, for example, exists in at least two tautomeric forms possessing the same melting point, one crystallising in needles and the other in granules. Several preparations of freshly crystallised needles have been administered to fourteen polyneuritic pigeons in doses of 1 to 2 mg., and in every case improvement or cure resulted. On the other hand, the granular form has been tested in doses of 0·5 to 100 mg. on some thirty birds under varying conditions, but without the slightest evidence of any benefit. The needle crystals, on keeping, pass into the granular form, especially in the presence of moisture. The reverse change can be effected by slowly cooling the melted substance, and then crystallising from benzene and light petroleum. The change from the granular to the needle form cannot apparently be achieved by the animal organism.

3- and 4-Hydroxypyridine and 4-lutidone have also been prepared. They also show curative properties only under certain conditions, and these curative properties automatically disappear with the lapse of time. Each crystallises in two different forms and forms metallic salts, which absorb bromine rapidly in cold alcohol in a manner strictly parallel to that of the corresponding salts of 2-hydroxypyridine.

These experiments suggest that the instability of the "vitamines" in foodstuffs is due to the occurrence of tautomeric changes of a nature similar to those described by the author.

H. W. B.

"Senso," the Dried Venom of the Chinese Toad. SHIGEMATSU SHIMIZU (*J. Pharm. Expt. Ther.*, 1916, **8**, 347—383).—"Senso" is a Chinese drug prepared from toad skins, and contains cholesterol and a crystalline substance which appears to be identical with bufagin (compare Abel and Macht, A., 1912, ii, 1193). Two other substances have also been isolated in an impure state, one of which resembles adrenaline and the other, named *bufotoxin*, appears to be a member of the picrotoxin group of poisons.

H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Occurrence of Chitin and Cellulose in Bacteria. C. VAN WISSELINGH (*Pharm. Weekblad*, 1916, **53**, 1070—1078, 1102—1107).—Chitin was absent from seventeen varieties of bacteria examined; cellulose was present only in *Bacterium xylinum*.

A. J. W.

Relations between the Chemical Constitution of Certain Derivatives of Amino-acids and the Method of Attack of the Latter by Bacteria. A. BLANCHETIÈRE (*Compt. rend.*, 1916, **163**, 206—209).—The author finds that when Flugge's fluorescent, liquefying bacteria act on asparagine in a given medium, nearly 50% of the theoretical yield of succinic acid is obtained. Emmerling and Reiser (compare A., 1902, ii, 279), on the other hand, found no succinic acid, but the production of fumaric acid, under similar conditions. Neuberg and Ringer having demonstrated the formation of oxalacetic acid when asparagine is attacked by certain bacteria (compare A., 1915, i, 1046), the author considers that this is the intermediate product in the attack by *Bacillus fluorescens* and is then converted either from its ketonic form, $CO_2H{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$, into succinic acid by reduction passing through malic acid, or from its enolic form,

$$CO_2H{\cdot}CH{:}C(OH){\cdot}CO_2H,$$

into fumaric acid. W. G.

Velocity of Scission of Lactose by the Action of the "Bulgarian Ferment." II. G. QUAGLIARIELLO and C. VENTURA (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 793—798. Compare this vol., i, 619).—The conversion of lactose into lactic acid by *Bacillus bulgaricus* is not a unimolecular reaction, the value of the velocity constant showing a continuous diminution as the action proceeds. With two samples of milk containing different proportions of lactose, the action ceased in each case when the concentration of the lactic acid formed became about 0·270 gram-mol. per litre, or about 2·5%, the bacteria apparently being incapable of vitality beyond this point. With an aqueous solution of lactose or with whey this maximal acidity has different values, but in all probability the hydrogen-ion concentration is the same in the three cases. T. H. P.

Nitrate and Nitrite Assimilation. VIII. Cholera. I. OSKAR BAUDISCH (*Ber.*, 1916, **49**, 1148—1158).—The awful toxic effects which so speedily manifest themselves in cholera are regarded by some serologists as being due to a bacterial toxin, a highly complicated protein. The life-history of the comma bacillus, however, is connected with a powerful oxidative degradation of proteins, and as these are broken down into amino-acids in the intestine, it is doubly unlikely that a very toxic protein would be rebuilt and enter the blood-stream in the presence of the bacillus. It is more reasonable to suppose, and there is evidence to this effect, that the toxic substances are among the degradation products of the vibrio. The cholera bacillus is now shown to be a particularly powerful producer of indole derivatives, especially from tryptophan, and also of nitrites, both from nitrates and from ammonia and amines. This has often been mentioned and often questioned in bacteriological literature, but the author regards it now as proved.

In the first place, it was attempted to show that the cholera

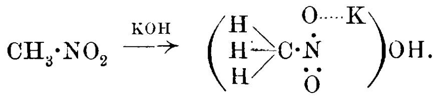
bacillus produces nitrites in a peptone culture free from nitrates or nitrites, that is, from amino-nitrogen. A culture was rendered faintly alkaline with sodium hydroxide and distilled under reduced pressure, the products being trapped in a cooled receiver and a series of wash-bottles. The distillate had the odour of indole and ammonia, and gave the intense red colour of "nitroso-indole" on acidifying. Nitrous acid could not be detected, however, except after extracting the indole with chloroform. This might have come from ammonium nitrite; but a second distillation from a much more alkaline medium, from which nitrites could not possibly escape, also gave a slight nitrite reaction in the first two receivers. The assumption is, therefore, that nitric oxide had passed over and become oxidised in the receivers, which is evidence of the formation of NOH, the intermediate product between ammonia and nitrous acid (compare A., 1913, i, 324, etc.). The existence of this in the cholera-peptone culture suggested that aldoximes or their products of oxidation, the nitriles, might also be present. In one distillation the vapours were trapped by means of water, and the presence of extremely volatile aldoximes was indeed demonstrated by adding indole and then an acid, when a violet-red colour developed (a new test for aldoximes; see next abstract). Also, on rendering a culture acid and leaving it to incubate a short time longer, hydrogen cyanide could be detected.

It has also been noticed frequently that cholera-peptone cultures containing a little alkali carbonate and a nitrate give particularly fine red to violet colours on acidifying, whilst Witte's peptone and nitrate solutions never give such brilliant and durable colorations. This points to the formation of indylmethane dyes, which give coloured salts with acids, from indole and the aldoximes, or possibly nitromethane, and the so-called cholera-red reaction is therefore not exclusively due to nitrosoindole.

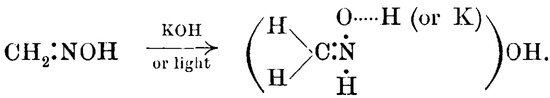
It cannot be said that cholera toxicity is due to the formation of hydrogen cyanide in the acid membrane of the small intestine, but the production of such volatile, poisonous substances as have been mentioned above does explain why a cholera-peptone culture loses its toxicity if heated at 100° in an open vessel, but not if heated at 120° in a closed one. J. C. W.

Nitrate and Nitrite Assimilation. IX. OSKAR BAUDISCH (*Ber.*, 1916, **49**, 1159—1167).—When an alkaline solution of an aldoxime is mixed with indole and then acidified, or when a neutral solution of an aldoxime is exposed to ultraviolet light for a few seconds, then mixed with indole, followed by an acid, a violet-red coloration develops. No colour appears if the oxime, however it has been treated, is acidified before adding the indole; that is, the reaction is one of a labile isomeride of the oxime which is favoured by alkalis or light. Nitromethane behaves similarly (A., 1915, i, 719), except that acids do not immediately change the labile into the stable form. This activity of nitromethane, and other transformations, oxidations, auto-oxidations, and condensations,

both at the nitrogen and the carbon atom, of which examples are discussed, is expressed to a certain extent by an ammonium salt formula of Werner, thus:



The indole dye would therefore be a mono-, di-, or tri-indylnitromethane, in analogy with the formation of the phenylnitromethanes from diazobenzene. The indole would, however, have to be oxidised first, probably to 2-hydroxyindole, a reaction of which labile nitromethane is capable. Similarly, the activities of labile formaldoxime could be represented thus:



The oxidation of indole by the loosely-held oxygen and the formation of a di-indylmethane dye would follow the same course as in the case of nitromethane. Such a formula would also account for the curious amine-like odour, reminiscent of bruised green plants, which is noticed during the action of ultraviolet light on the oxime, and also the building up of a pyrrole ring when the oxime and formaldehyde are illuminated together (A., 1913, i, 324).

The photochemical changes which these compounds suffer under the continued action of light can also be realised when nascent hydrogen peroxide is applied to them. This can be accomplished by adding oxanthrone to feebly alkaline solutions, and a number of cases are described in which the effect is the same as if the compounds had been illuminated.

The rôle of the aldoximes in plant metabolism is an important subject that needs to be investigated fully, and the possible activities of the labile forms of these compounds need only to be realised in order to indicate the magnitude of the problem. J. C. W.

Nitrate and Nitrite Assimilation. X. OSKAR BAUDISCH and GABRIEL KLINGER (*Ber.*, 1916, **49**, 1167—1176).—It has frequently been shown that oxidation by peroxides and reduction by hydrogen can proceed side by side in photochemical changes (compare A., 1911, ii, 523; 1912, ii, 286, 1202). The presence of a metal which "activates" hydrogen would therefore greatly influence a photochemical reaction in the direction of the reduction. For example, when a solution of formaldehyde and potassium nitrite, with or without magnesium carbonate, is exposed to daylight or ultraviolet light, the chief gaseous products are hydrogen and nitrous oxide, whereas by the substitution of magnesium nitrite for the potassium salt the hydrogen disappears and nitrogen appears at the expense of the nitrous oxide. This great influence of the magnesium would seem to be due to a complex salt which might well be formed in a solution of magnesium nitrite containing

formaldehyde. It appears to be certain that peroxides, side by side with activated hydrogen, play the chief part in the photosyntheses of plants, and the magnesium in the chlorophyll molecule may well be the activating agent. J. C. W.

Nitrate and Nitrite Assimilation. XI. OSKAR BAUDISCH (*Ber.*, 1916, **49**, 1176—1182).—Many of the photochemical experiments with nitrates and nitrites have shown that the old formulæ for these salts, $MO{\cdot}N{\lessdot}\begin{smallmatrix}O\\O\end{smallmatrix}$ and $MO{\cdot}N{:}O$ or $MN{\lessdot}\begin{smallmatrix}O\\O\end{smallmatrix}$, are insufficient to interpret the results. For example, if nitric oxide is exposed to ultraviolet light over water, ammonium nitrite, but no nitrate, is formed; similarly, with a mixture of dry ammonia and an excess of oxygen the oxidation ceases at the nitrite stage. In the presence of an oxygen carrier, however, nitrates are formed; thus, nitric oxide over water, in the presence of yellow phosphorus, yields ammonium nitrate, and a solution of potassium nitrite mixed with methyl alcohol gives ammonia and potassium nitrate, which separates in large crystals. Conversely, nitrates are easily reduced to nitrites by illumination; even in an oxygen atmosphere potassium nitrate yields the nitrite. A starch–potassium iodide solution containing a nitrate soon becomes blue on illumination, owing to the liberation of active oxygen, whereas a nitrite solution does not become blue, but develops an odour of iodoform. These and other reactions are discussed on the basis of Werner's formulæ for nitrates and nitrites.

Under the action of light, potassium nitrate, for example, would combine with water, thus, $K\left\{\begin{matrix}O\\ NO\cdots\\ O\end{matrix}\right\} \longrightarrow K\left\{\begin{matrix}O\\ NO\cdots OH_2\\ O\end{matrix}\right\}$, and oxygen would then be split off, two atoms uniting to form a gaseous molecule in the absence of any powerful reducing agent. In a nitrite, however, the oxygen is combined as a peroxide, and water would be attached, and then eliminated as a nascent peroxide, thus:

$$K\left\{\begin{matrix}O\\ \overset{:}{N}\\ \overset{\cdot\cdot}{O}\end{matrix}\right\} \longrightarrow K\left\{\begin{matrix}O\cdots H\\ \overset{\cdot}{N}{\cdot}OH\\ \overset{\cdot\cdot}{O}\end{matrix}\right\} \longrightarrow K(NO)+H_2O_2.$$

This explains why easily oxidisable substances are so rapidly oxidised by nitrites in the light. The residue, K(NO) or H(NO), would immediately break down into NO and H, which explains the formation of hydroxylamine and ammonia when potassium nitrite solutions are exposed to intense ultraviolet light.

The behaviour of the free acids towards oxygen is quite another matter, the oxygen in them being of exceptional mobility. Thus, nitric oxide in the presence of moisture and air easily reaches the stage of nitric acid, but potassium nitrite is not oxidised even in the presence of a great excess of oxygen. J. C. W.

Effect of Soil Reaction on Ammonification by Certain Soil Fungi. NICHOLAS KOPELOFF (*Soil Sci.*, 1916, **1**, 541—573).—*Rhizopus nigricans*, *Zygorrhyncus Vuilleminii*, and *Penicillium* are

equally affected by changes in the reaction of the soil; such changes have a greater effect when dried blood is employed than with cottonseed meal, and in clay soils as compared with sandy soils.

The maximum accumulation of ammonia by these fungi occurs between the neutral point and an acidity equivalent to 2000 lb. of calcium oxide per acre. Acidity greater than this, and an increase in alkalinity beyond the neutral point, generally cause a depression in ammonia production.

It is suggested that ammonification by fungi may be of practical importance under conditions unfavourable to soil bacteria.

N. H. J. M.

Protein Decomposition in Soils. ELBERT C. LATHROP (*Soil Sci.*, 1916, **1**, 509—532).—A sandy loam soil was thoroughly mixed with dried blood (40 : 4) and kept for two hundred and forty days in a jar covered with perforated paper. The percentage of water in the soil was kept at 10%, water being added at intervals of five to eight days, when the soil was turned out and mixed to promote aeration. Samples were taken for estimating the different forms of nitrogen after eighteen, forty-four, eighty-six, one hundred and forty-eight, and two hundred and forty days.

Ammonification was very rapid during the first eighty-six days, after which there was a marked fall until the end of the experiment, when the production of ammonia was only at about 10% of the rate observed after the first eighteen days. In two hundred and forty days 79% of the blood proteins was converted into ammonia. Of the nitrogen of the monoamino-acids about 89% was converted into ammonia, whilst argenine and histidine each gave about 83%.

Indications were obtained that new protein substances were formed, and that these are more resistant to the action of micro-organisms than the proteins of dried blood. The lysine of the dried blood disappeared almost completely in eighty-six days, whilst during the last one hundred and fifty-four days there was a continual increase in this form of nitrogen.

At the end of two hundred and forty days the soil contained protein-like substances soluble in 1% sodium hydroxide. It is uncertain whether these substances form undecomposed residues of the dried blood, or whether they are newly formed proteins.

N. H. J. M.

Effect of some Manganese Salts on Ammonification and Nitrification. P. E. BROWN and G. A. MINGES (*Soil Sci.*, 1916, **2**, 67—85).—The soil employed was a clay loam, containing 0·1732% of manganese. In the ammonification experiments the soil received 5% of dried blood, whilst for nitrification 0·1 gram of ammonium sulphate was added.

Manganese chloride, applied at the rate of more than 2000 lb. per acre, retarded both ammonification and nitrification. Applications of 100 and 200 lb. increased ammonification slightly and nitrification distinctly. Manganese sulphate increased both ammonifica-

tion and nitrification when applied at the rate of 100 lb. per acre, whilst large amounts (2000 lb.) have a depressing effect.

Manganese oxide applied at the rate of 2000 lb., or more, per acre retards both ammonification and nitrification. N. H. J. M.

Citric Acid by Fermentation. JOHN ALBERT MARTIN (*Amer. J. Pharm.*, 1916, **88**, 337—355).—Certain fungi of the *Ascomycetes* group, when grown on a neutral or slightly acid sugar solution, produce citric acid. The production of acid is gradual, and ceases when the amount is about 20% of the sugar employed. By neutralising the acid with calcium carbonate, the yield can be increased to 50% of the sugar.

An excess of air is necessary for the fermentation.

N. H. J. M.

Decrease of Permeability Produced by Antiseptics. W. J. V. OSTERHOUT (*Bot. Gaz.*, 1916, **61**, 149—158).—The results of experiments with tissues of *Laminaria saccharina* showed that when placed in sea-water and ether the permeability first increases and then decreases; the effect can be readily reversed by placing the tissues in sea-water. The increase of permeability produced by ether is not reversible. Similar results were obtained with chloroform and with chloral hydrate. With alcohol the increase of permeability is reversible. N. H. J. M.

Determination of Additive Effects. W. J. V. OSTERHOUT (*Bot. Gaz.*, 1915, **60**, 228—234).—Two solutions which are equally toxic generally remain equally, or nearly equally, toxic when diluted to the same degree; this enables the additive effect readily to be determined.

In exceptional cases, when this does not hold, a value may be assigned to the additive effect. Similar considerations apply to unequally toxic solutions. N. H. J. M.

Action of Lead as a Stimulant for Plants. A. STUTZER (*J. Landw.*, 1916, **64**, 1—8).—The results of water culture experiments with rye, wheat, oats, barley, maize, and peas showed better growth when a portion of the nitrogen was in the form of lead nitrate than with sodium nitrate only. The best plants, especially barley, were obtained in solutions containing 0·5 gram of lead nitrate per litre.

In field experiments the yields of sugar beet and of sugar were considerably increased by application of 4 kilos. of lead nitrate per hectare. With oats the yield of grain was increased, whilst the yield of straw was diminished. The same amount of lead nitrate (4 kilos. per he.) gave unsatisfactory results with potatoes, which seem to be very sensitive to lead nitrate.

Another field experiment, with wheat, showed that whilst lead nitrate gave good results in conjunction with 50 kilos. of nitrogen as sodium nitrate, the results were much less satisfactory when smaller amounts of sodium nitrate were employed. N. H. J. M.

Organic Chemistry.

The Thermal Decomposition of the Ethane–Propane Fraction from Natural Gas Condensate. J. E. ZANETTI and E. H. LESLIE (*J. Ind. Eng. Chem.*, 1916, **8**, 777—779).—The thermal decomposition of an ethane–propane mixture obtained from a natural gas condensate was studied in the same manner as that of the propane–butane fraction previously described (this vol., i, 625). The products consisted of ethylene, propylene, and other unsaturated hydrocarbons, hydrogen, and aromatic hydrocarbons, the proportion of the unsaturated hydrocarbons reaching a maximum at about 750°, at which temperature the formation of aromatic hydrocarbons begins, and is accompanied by an increase in the rate of formation of hydrogen. The tar obtained, 2·5 c.c. per cubic foot of gas used, had D 1·075, and on distillation 20 c.c. gave 3 c.c. up to 125°, 1 c.c. up to 200°, and a residue of naphthalene and pitch. From the lower fraction nitrobenzene, but no nitrotoluene, was obtained. The use of iron as a catalyst in the heating chamber prevented the formation of aromatic hydrocarbons and favoured decomposition into carbon and hydrogen. The effect of copper as catalyst was not marked in any way. G. F. M.

Comparative Experiments on the Hydrogenation of Oils, using Metallic Nickel and Nickel Oxides. W. NORMAN (*Chem. Zeit.*, 1916, **40**, 757—759).—Metallic nickel, without a carrier (for example, kieselguhr) acts quite satisfactorily for the hydrogenation of oils on a commercial scale. Certain nickel oxides, when reduced, yield a metal which is inferior in its action to that of the oxide, but, under working conditions, the metal is generally superior to the oxide as a catalyst. Statements as to the effect of impurities on the sensitiveness of the metallic catalyst are partly exaggerated, partly untrue. W. P. S.

Halogenation. XII. Formation of Chloropicrin and Tetrachloroquinone by the Action of Aqua Regia on Organic Substances. RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1916, **38**, 1813—1821).—In an earlier paper (A., 1915, i, 114) the authors have shown that some organic substances are decomposed by aqua regia with formation of chloropicrin. An account is now given of experiments with a large number of organic compounds, which have led to the generalisation that whenever an organic compound is decomposed destructively by aqua regia, chloropicrin is produced. In some cases, a quantitative yield of chloropicrin is obtained; in other cases, moderate quantities are produced, and sometimes only traces are formed. The chloropicrin is often accompanied in these reactions by very small quantities of other chloronitro-derivatives of methane. In the case of certain aromatic compounds, chloranil [tetrachloro-*p*-benzo-

quinone] is produced, but as this yields chloropicrin under the influence of aqua regia, chloropicrin is always formed in such decompositions.

Datta (A., 1914, i, 701) has shown that chloranil can be prepared by the action of aqua regia on *p*-phenylenediamine or quinol. It has now been found that trichlorophenol and sulphanilic acid also give good yields of chloranil, and that as sulphanilic acid can be obtained cheaply it is the most economical substance for the manufacture of chloranil on the large scale. The following yields have been obtained by the action of aqua regia on 20 grams of each of these compounds: *p*-phenylenediamine, 13—14 grams; quinol, 13—14 grams; trichlorophenol, 10 grams; and sulphanilic acid, 6—7 grams. E. G.

The Hydrocarbons of Beeswax. HUGH RYAN and THOMAS DILLON (*Sci. Proc. Roy. Dublin Soc.*, 1916, [ii], **15**, 107—112).—After a historical survey of the chemistry of beeswax, the authors show that in the procedure adopted by Buisine and Buisine (A., 1891, 131) for the estimation of the hydrocarbons in beeswax by heating with potash-lime, and extracting the residue with light petroleum, the reaction is not quite complete, a small proportion of the primary alcohols escaping conversion into the corresponding acids; also if there should be traces of secondary or tertiary alcohols present these would probably fail to react with the potash-lime, and so also be included in the hydrocarbons. Indeed, analysis of the "hydrocarbons" extracted by light petroleum reveals the presence of an appreciable percentage of oxygen.

In experiments with alcoholic substances, it is shown that in the case of melissyl alcohol at 250° only 95·9% reacts with potash-lime, yielding hydrogen, whilst dimethylheptadecylcarbinol, diphenylheptadecylcarbinol, and *p*-tolylpentadecylcarbinol at the same temperature yield no hydrogen at all. Dextrose at 250° gives rise to rather less hydrogen than corresponds with its single primary hydroxyl group. D. F. T.

Mixed Xanthic Anhydrides. M. M. RICHTER (*Ber.*, 1916, **49**, 1026—1029).—The reaction between thionyl chloride and salts of organic acids, which gives rise to acid chlorides, probably takes place in two stages, as shown by the equations: (1) $2CH_3{\cdot}CO_2Na + SOCl_2 = (CH_3{\cdot}CO_2)_2SO + 2NaCl$, (2) $(CH_3{\cdot}CO_2)_2SO + SOCl_2 = 2CH_3{\cdot}COCl + 2SO_2$. The intermediate mixed anhydride of acetic and sulphurous acids cannot be isolated during the reaction, but the author has satisfied himself that this compound, when prepared from acetyl chloride and lead sulphite (compare Tommasi, *Ber.*, 1874, **7**, 826), reacts according to the second equation given above when heated with thionyl chloride.

When xanthates are used the reaction with thionyl chloride stops at the first stage, in accordance, for example, with the equation: $2EtO{\cdot}CS{\cdot}SK + SOCl_2 = (EtO{\cdot}CS{\cdot}S)_2SO + 2KCl$; excess of thionyl chloride does not give rise to the acid chloride.

The mixed anhydrides thus produced cannot be distilled, since

they decompose at 40—45°, liberating carbon disulphide; for example, $EtO·CS_2·COMe = CS_2 + Me·CO_2Et$. It is therefore necessary specially to purify all the materials used in their preparation, and also to take great care to exclude moisture and alcohol. The acid chloride is dissolved in eight to ten times the quantity of carbon disulphide and treated, under cooling, with a little more than the calculated quantity of the xanthate, which is added in small portions at a time; the temperature must not exceed 30°. After collecting the precipitated potassium chloride, the carbon disulphide is removed under diminished pressure (15 mm.), the temperature not exceeding 30°. The anhydride thus obtained is practically pure, but may contain traces of ethyl sulphite.

All the anhydrides prepared are golden-yellow, highly refracting liquids possessing a peculiar and often penetrating, mercaptan-like odour.

Ethylxanthic-sulphurous anhydride, $(EtO·CS_2)_2SO$, has an intense odour of sulphurous acid. With aniline, it gives xanthanilide and diphenylthiocarbamide. It is very sensitive towards alkalis, the alkali of the glass vessel containing it turning it cloudy in a few days. *Methylxanthic-sulphurous anhydride*, $(MeO·CS_2)_2SO$, has similar properties, but forms crystals which melt with the warmth of the hand.

Ethylxanthic-phosphoric anhydride, $(EtO·CS_2)_3PO$, is prepared by using phosphoryl chloride, and has an unpleasant odour. *Ethylxanthic-acetic anhydride*, $EtO·CS_2·COMe$, has a mercaptan-like odour, whereas *ethylxanthic-benzoic anhydride*, $EtO·CS_2·COPh$, and *ethylxanthic-benzenesulphonic anhydride*, $EtO·CS_2·SO_2Ph$, are practically odourless. T. S. P.

Normal Ammonium Salts of some Organic Acids and their Substituted Derivatives. VI. LE ROY MCMASTER and A. C. MAGILL (*J. Amer. Chem. Soc.*, 1916, **38**, 1785—1803).—In earlier papers (Keiser and McMaster, A., 1913, i, 248; McMaster, A., 1913, i, 444; 1914, i, 481, 1122; McMaster and Godlove, A., 1915, i, 958) normal ammonium salts of various organic acids have been described which were prepared by passing dry ammonia into solutions of the acids in the organic solvents, methyl alcohol, ethyl alcohol, ether, acetone, and benzene. In the work now described, ethyl acetate was used in some cases.

The preparation has been effected of ammonium *tribromoacetate*, *phenylbromoacetate*, o-*nitrophenylacetate*, *phenylaminoacetate*, glycollate, *α-bromopropionate*, *β-iodopropionate*, *β-chlorolactate*, trichlorobutyrate, octoate, decoate, *laurate*, *myristate*, *α-bromopalmitate*, *α-bromostearate*, *acrylate*, *β-chlorocrotonate*, *erucate*, *dimethylmalonate*, *dipropylmalonate*, iso*propylmalonate*, *butylmalonate*, *allylmalonate*, *benzylmalonate*, *bromosuccinate*, dibromosuccinate, suberate, and chlorofumarate. E. G.

Catalysis. I. Additive Compounds of Esters with Organic Acids. JAMES KENDALL and JAMES ELIOT BOOGE (*J. Amer. Chem. Soc.*, 1916, **38**, 1712—1736).—The catalysis of ester hydrolysis by

acids is now generally explained on the theory of the formation of intermediate additive compounds, but no conclusive evidence of the presence of such compounds has hitherto been obtained. The authors have therefore undertaken a systematic study of the general behaviour of mixtures of esters and acids with respect to the formation of additive compounds (oxonium compounds).

The examination of twenty-two ester-acid systems has been carried out by the f. p. method employed by Kendall in earlier work (A., 1914, i, 858, 1069; 1915, i, 80; this vol., i, 599). The results of this earlier work showed that oxonium compounds are more readily formed when the acidic strengths of the two components vary widely. Similarly, in the present case, it has been found that combination is most marked between strong acids and esters of weak acids. The extent of compound formation decreases rapidly with decrease in the strength of the acid, but is still perceptible with so weak an acid as acetic, and the conclusion is therefore drawn that oxonium salt formation is a general phenomenon in ester-acid systems. These results accord with the facts that acids, in general, accelerate ester hydrolysis, and that the acceleration decreases with decrease in the strength of the acid.

The following compounds of esters with trichloroacetic acid have been isolated, each compound consisting of 1 mol. of each of the components: ethyl acetate *compound*, m. p. $-27·5°$, large, lustrous plates; α-naphthyl acetate *compound*, m. p. $10·7°$, prismatic needles; β-naphthyl acetate *compound*, m. p. $66·3°$, thin, oblong plates; ethyl benzoate *compound*, m. p. $-23·4°$, needles; the methyl benzoate *compound* crystallises in two modifications, m. p. $-10·6°$ and $-8·8°$; benzyl benzoate *compound*, m. p. $11·9°$, needles; methyl anisate *compound*, m. p. $-6·3°$, small, lustrous plates; methyl cinnamate *compound*, slender needles; methyl *p*-toluate *compound*, m. p. 9°, rectangular plates.

The following compounds containing 1 mol. of the ester and 2 mols. of trichloroacetic acid were also isolated: methyl succinate *compound*, m. p. 8°, slender prisms; methyl malonate *compound*, m. p. $-28·5°$, plates; ethyl oxalate *compound*, m. p. $3·4°$, thin plates.

The methyl terephthalate *compound*,

$$C_6H_4(CO_2Me)_2,4CCl_3·CO_2H,$$

m. p. $27·9°$, forms large needles.

The m. p.'s of the following esters are recorded: ethyl benzoate, m. p. $-32·7°$; methyl benzoate has m. p. $-12·3°$, and a metastable, crystalline form, m. p. $-13·7°$, also exists; methyl cinnamate, m. p. $34·7°$; methyl *p*-toluate, m. p. $33·2°$; ethyl malonate, m. p. $-62°$. E. G.

[Sodium Calcium Lactate.] J. A. Wülfing (Eng. Pat., 1915, 17274; from *J. Soc. Chem. Ind.*, 1916, **35**, 907).—A sodium calcium lactate of the composition $2C_3H_5O_3Na,(C_3H_5O_3)_2Ca,4H_2O$ is obtained by mixing 238 grams of calcium lactate containing 9% of water with 280 grams of sodium lactate syrup containing 20% of water. The mixture gradually solidifies, and the resulting non-

hygroscopic double salt is very suitable for the administration of calcium to the human system. G. F. M.

Cerebronic Acid. V. Relation of Cerebronic and Lignoceric Acids. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1916, **26**, 115—120).—It was originally supposed that cerebronic acid was a *n*-α-hydroxypentacosoic acid (A., 1912, i, 936; 1913, i, 587), which view is also held by Thierfelder and Brigl. In a recent paper (this vol., i, 463), Brigl criticised the authors' methods of proof, but his own conclusions were not more successful. It is now pointed out that the original view has been modified in the meantime. Cerebronic acid is regarded as the α-hydroxy-derivative of the next higher homologue of lignoceric acid, which is not a normal acid, but a tetracosoic acid with a branched chain (compare A., 1914, i, 1123). The authors indicate how they hope to prove this. J. C. W.

Action of a Solution of Potassium Hydroxide in Alcohol on Oxalic Esters. N. C. QUA and D. McLAREN (*J. Amer. Chem. Soc.*, 1916, **38**, 1803—1809).—Experiments on the action of alcoholic potassium hydroxide (1 mol.) on dialkyl esters (1 mol.) have been carried out with the following results. Alkyl oxalates gave potassium alkyl oxalate; alkyl tartrates yielded potassium alkyl tartrate and a little potassium tartrate; alkyl succinates gave potassium alkyl succinate and large quantities of potassium succinate; and alkyl phthalates furnished potassium phthalate only.

Further experiments with alkyl oxalates have shown that when these esters are treated with slightly less than the calculated amount of potassium hydroxide dissolved in an alcohol, a potassium alkyl oxalate is produced in which the alkyl radicle is that of the particular alcohol used; thus, for example, when ethyl oxalate is treated with a solution of potassium hydroxide in methyl alcohol, potassium methyl oxalate is obtained. It has been found that these results do not depend on the relative insolubility of the possible potassium salts. If ethyl oxalate is treated with much less than the calculated quantity of potassium hydroxide, the residual alkyl ester contains methyl oxalate in amount depending on the quantity of potassium hydroxide used. It is considered that the conversion of ethyl oxalate into potassium methyl oxalate is due to (1) the change of ethyl oxalate to methyl oxalate, and (2) the change of methyl oxalate to potassium methyl oxalate. The addition of potassium ethyl oxalate to a solution of ethyl oxalate in methyl alcohol does not result in the formation of any methyl oxalate. Experiments in which solutions of potassium hydroxide in methyl alcohol containing varying amounts of water were added to ethyl oxalate showed that much less methyl oxalate is formed when water is present, and that the reaction is therefore due to potassium methoxide rather than to potassium hydroxide. E. G.

Bile Acids. II. Choleic Acid. HEINRICH WIELAND and HERMANN SORGE (*Zeitsch. physiol. Chem.*, 1916, **97**, 1—27. Compare Wieland and Weil, A., 1912, i, 830).—The authors bring evidence to show that choleic acid is a compound of deoxycholic acid and a fatty acid (palmitic, stearic, or oleic acid) in the proportion of 8 molecules of the former to 1 of the latter (compare Pregl, A., 1910, i, 321). On boiling choleic acid with glacial acetic acid for a few minutes and then cooling, *acetic choleic acid*,

$$C_{24}H_{40}O_4,C_2H_4O_2,$$

is obtained in crystalline form, m. p. 144—146°. Similar compounds can be prepared containing ether, ethyl acetate, or acetone instead of acetic acid. In each case the small molecular component is held tenaciously, and can only be partly removed by heating in a high vacuum for several days at 130°. The compounds are crystalline and odourless.

Pure deoxycholic acid, m. p. 172°, $[\alpha]_D^{20}$ +57·02, is obtained by crystallisation of the choleic acid from alcohol, followed by subsequent heating in a vacuum at 110°. Ethyl deoxycholate crystallises in needles, m. p. 81°, $[\alpha]_D^{20}$ +49·66. Oxidation of deoxycholic acid or of choleic acid yields the same dehydrocholic acid, m. p. 188—189°, $[\alpha]_D^{20}$ +92·09.

The ordinary choleic acids can be prepared by cooling a hot mixture in alcohol of deoxycholic acid and the respective fatty acid. Stearic–choleic acid has m. p. 186—187°, $[\alpha]_D^{20}$ +49·11°; palmitic–choleic acid, m. p. 184—185°; oleic–choleic acid, m. p. 185—186°. A mixture of equal parts of these three choleic acids in alcohol yielded, on cooling, crystals, m. p. 185—186°. The following *compounds* have also been prepared: (i) with hexoic acid,

$$(C_{24}H_{40}O_4)_5,C_8H_{16}O_2,$$

m. p. 170—172°; (ii) with butyric acid, $(C_{24}H_{40}O_4)_4,C_4H_8O_2$, m. p. 170° (not sharp); (iii) with propionic acid, $(C_{24}H_{40}O_4)_3,C_3H_6O_2$, m. p. 168° (not sharp); (iv) with benzene, m. p. 164°; (v) with xylene, $(C_{24}H_{40}O_4)_2,C_8H_{10}$, needles, m. p. 183°; (vi) with naphthalene, $(C_{24}H_{40}O_4)_2,C_{10}H_8$, glittering needles, m. p. 182°. H. W. B.

Reversible Replacement of Alcohols in Aldehyde-alcoholates. MARGUERITE WILLCOX and ROGER F. BRUNEL (*J. Amer. Chem. Soc.*, 1916, **38**, 1821—1841).—The authors point out that in order to obtain any accurate knowledge of the relation between chemical affinity on the one hand, and constitution and composition on the other, it is necessary that a study should be made of reversible reactions between comparatively simple substances in which the constitution of only one of the compounds is allowed to change. A further investigation has therefore been made of the reaction between alcohols and chloral-alcoholates (compare Gadamer, A., 1905, i, 326; Kuntze, A., 1908, i, 322). When chloral *l*-amyl-alcoholate is treated with any aliphatic alcohol, a reaction of the following type takes place:

$$CCl_3\cdot CH(OH)\cdot O\cdot C_5H_{11} + R\cdot OH \rightleftharpoons CCl_3\cdot CH(OH)\cdot OR + C_5H_{11}\cdot OH,$$

the optically active alcohol being partly displaced from its compound with the aldehyde by the other alcohol.

Two series of experiments have been carried out, in which (1) chloral *l*-amyl-alcoholate, and (2) butylchloral *d-sec.*-butyl-alcoholate respectively were treated with twenty-two inactive alcohols, and the course of the reaction followed polarimetrically. The determinations were made in benzene solution at 25°. It was found that the equilibrium point of the reaction varies with the alcohol used, but that the order in which the alcohols fall is not quite the same in the two series.

The results are discussed with regard to the affinities between the radicles concerned, and an attempt is made to establish a relationship between the constitution of the alcohol radicles and the end-point attained in the reactions.

The degree of dissociation of chloral ethyl-alcoholate into its constituents has been determined in benzene for a wide range of concentrations, and also, but in fewer concentrations, in bromoform, ethylene dibromide, and nitrobenzene. The results show that it is dissociated in dilute solutions, but associated in more concentrated solutions. In solutions of 5% strength, association predominates. There does not seem to be any relation between the degree of dissociation and the dielectric constant of the solvent.

E. G.

Chemico-analytical Definition of the Sugars. H. C. Milius and N. Schoorl (*Pharm. Weekblad*, 1916, **53**, 1249—1262).—An attempt to classify the sugars according to constitution and reducing power. The "open" sugars are aldols or ketols with the power of reducing certain substances. The "closed" sugars are transformed into "open" sugars by hydrolysis. Benzoylcarbinol and benzoin are classed as aromatic "open" sugars. A. J. W.

Biochemical Synthesis of α-Propyl-*d*-galactoside by means of a Ferment contained in the Air-dried Bottom Yeast of Beer. Em. Bourquelot and A. Aubry (*Compt. rend.*, 1916, **163**, 312—315; and *J. Pharm. Chim.*, 1916, [vii], **14**, 193—199).—α-Galactosidase is much less sensitive to the toxic action of propyl alcohol than is α-glucosidase (compare A., 1914, i, 144), and thus more concentrated solutions could be used for this synthesis. The aqueous solution contained 1% of galactose, 25% of propyl alcohol, and 20% of a 20% maceration of air-dried bottom yeast. The mixture was allowed to remain at the ordinary temperature for eight months, and from the resulting liquid by the processes employed for other galactosides, *α-propyl-*d*-galactoside* was finally isolated as long, narrow, colourless, odourless plates, m. p. 134° (corr.); $[\alpha]_D^{21}$ +179·04°. It is very soluble in water, and is readily hydrolysed by boiling it with dilute sulphuric acid or by the action of a maceration of the yeast on its aqueous solution. W. G.

Optical Rotatory Powers of some Acetylated Derivatives of Maltose, Cellose, and Lactose. C. S. Hudson and Ralph Sayre (*J. Amer. Chem. Soc.*, 1916, **38**, 1867—1873).—The specific rotations of α- and β-hepta-acetylmethylmaltosides have been calculated

by Hudson and Dale's method (A., 1915, i, 501; this vol., i, 597), and found to be $+138°$ and $+55°$ respectively. Determinations of the specific rotation of this substance in chloroform have given the value $[\alpha]_D^{20}$ $+54°$, which shows that the known form of the compound is the β-modification. By the same method of calculation, α- and β-hepta-acetylmethylcellosides were found to have $[\alpha]_D$ $+56°$ and $-28°$ respectively. The known form of this compound gives $[\alpha]_D^{20}$ in chloroform $-25·4°$, and is therefore the β-form.

α- and β-Hepta-acetylmaltoses gave the calculated values for $[\alpha]_D$ $+131°$ and $+66°$ respectively; the experimental value of the β-form in chloroform was $[\alpha]_D^{20}$ $+67·8°$. α- and β-Hepta-acetylcelloses similarly gave the calculated values $+46°$ and $-19°$. Hepta-acetylcellose, prepared from acetylbromocellose, gave, after repeated recrystallisation, the value $[\alpha]_D^{20}$ in chloroform $-2°$, and by continued purification would probably have given a lower figure. α- and β-Hepta-acetyllactoses gave the calculated values $+59°$ and $-6°$. *Hepta-acetyllactose*, m. p. 83° (corr.), prepared from acetylbromolactose, gave $[\alpha]_D^{20}$ in chloroform $-0·3°$ after twenty recrystallisations, but even then a constant value was not attained. E. G.

Chondrosamine. P. A. LEVENE (*J. Biol. Chem.*, 1916, **26**, 143—154. Compare A., 1914, i, 889; 1915, i, 601, 944).—The supposed similarity between the osazones of chondrosamine and altrose, coupled with the fact that lyxohexosamic acid and chondrosamic acid yielded apparently different anhydrotetrahydroxyadipic acids on oxidation, led the author to believe that chondrosamine was a ribosimine rather than a lyxohexosamine. The purified osazone is now found to be identical with galactosazone, both in m. p. and in the nature of its mutarotation, and both amino-acids are found to yield the same anhydromucic acid on oxidation. Chondrosamine is therefore more probably a lyxohexosamine. A lyxohexosamine has now been prepared from lyxohexosamic acid (following abstract), but it is not identical with chondrosamine, although it forms the same osazone. Thus there are two different amino-sugars which yield the same osazone, and two different α-hexosamic acids which form the same anhydromucic acid on oxidation. The natural assumption to make is, therefore, that the two pairs of substances are epimeric, one conforming to galactosamine and the other to talosamine, but the isomerism is not quite so simple. If chondrosamine is de-aminised and then oxidised by bromine, it apparently forms the same acid that lyxohexosamic acid yields when de-aminised. The substance, chondronic or anhydrotalonic (?) acid, has been isolated as a *brucine* salt, $C_{29}H_{26}O_{10}N_2$, m. p. 218° (corr.), decomp. 223°, $[\alpha]_D^{20}$ $-12·4°$ (not $+$, as was wrongly stated in the 1914 paper). On the other hand, if chondrosamic acid is de-aminised, it yields a different monocarboxylic acid, *epi*chondronic or anhydrogalactonic (?) acid, the *brucine* salt of which crystallises in long, heavy prisms, m. p. 244° (corr.), $[\alpha]_D^{20}$ $-9·23°$.

Chondrosamine has been converted by the hydrogen cyanide synthesis into *chondrosaminoheptonic acid*, $C_7H_{15}O_7N,H_2O$, which formed rosettes of long, pointed prisms, m. p. 136° (corr.),

$[\alpha]_D^{20}$ $-14\cdot40°$ (in 2·5% hydrochloric acid). The purification of the acid was a matter of great difficulty, and it involved the formation of the *copper* salt.

Details are given of an expeditious method for obtaining chondrosamine from nasal septa, the yield of the hydrochloride being nearly 40 grams from 20 lb. of material. J. C. W.

Synthesis of Hexosamines. I. P. A. LEVENE (*J. Biol. Chem.*, 1916, **26**, 155—162).—The synthesis of all the possible hexosamines offers exceptional difficulties. When the hydrogen cyanide synthesis is applied to the pentosimines, it invariably happens that only one hexosamic acid can be isolated, and the subsequent reduction of the lactones of these by means of sodium amalgam usually leaves the desired product contaminated with sodium salts and unreduced material. Glucosamine derivatives have been prepared, however, by Fischer and Leuchs (A., 1910, i, 233), but a slight improvement in their method, namely, reduction by means of sodium amalgam in a hydrochloric acid solution, has enabled the author to obtain both glucosamine and lyxohexosamine more easily.

For the preparation of the lactones it was necessary to use the very pure hexosamic acids. Glucosamic acid yielded directly a fraction of glucosamine hydrochloride containing only about 2% of salt and representing about 50% of the total sugar. From this, pentabenzoylglucosamine, m. p. 216°, $[\alpha]_D^{20}$ $+44\cdot4°$, could be obtained pure. Xylohexosamic acid gave poor results, but *pentabenzoylxylohexosamine*, $C_6H_8O_5NBz_5$, was isolated in white needles, m. p. 162°, $[\alpha]_D^{20}$ $+77\cdot6°$, and an *osazone*, $C_{18}H_{24}O_4N_4$, was also obtained in lemon-yellow, curved needles, m. p. 173° (corr.), decomp. 185°. Better results were obtained with lyxohexosamic acid. *Lyxohexosamine hydrochloride*, $C_6H_{13}O_5N,HCl$, crystallised in long prisms, m. p. 185° (corr.), $[\alpha]_D^{25}$ $+62\cdot69°$ (initial) $+91\cdot10°$ (equilibrium), and yielded the same osazone as chondrosamine and galactose, m. p. 201° (corr.). J. C. W.

Influence of Neutral Salts on the Solubility of Amino-acids. P. PFEIFFER and J. WÜRGLER (*Zeitsch. physiol. Chem.*, 1916, **97**, 128—147).—The influence of neutral salts on the solubility of amino-acids is similar to that exerted on proteins. In each case cations and anions have an additive action. If the ions be arranged in the order corresponding with the effect produced on the solubility of the amino-acid, we have the series $NO_3>I>Br>Cl$; $Li>Na>K$; $Ca>Sr,Ba$ in the case of neutral amino-acids, such as glycine, and the series $NO_3>I>Br>Cl$; $K>Na>Li$; $Ba>Sr>Ca$ in the case of acid amino-acids, such as aspartic acid. The characteristic action of salts on the solubility of proteins is due, therefore, not to the colloidal condition of the latter, but to their amino-acid structure. H. W. B.

Compounds of Amino-acids and Ammonia. VIII. PETER BERGELL (*Zeitsch. physiol. Chem.*, 1916, **97**, 293—306).—The

amides of dipeptides are formed by the action of ammonia on a new series of compounds prepared by the interaction of glycinamide and different amino- or corresponding halogen acids.

On shaking glycinamide with bromopropionyl bromide in alkaline solution at 0°, *a-bromopropionylglycinamide*,

$$CHMeBr\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2,$$

is formed, which crystallises from alcohol in long prisms and rhombohedrons, m. p. 162°. On treatment with aqueous ammonia, the expected dipeptide-amide, if formed, is hydrolysed so rapidly that it cannot be isolated; instead, a small quantity of the corresponding anhydride, diketomethylpiperazine, is obtained. When bromo*iso*valerylbromide is employed, *a-bromo*iso*valerylglycinamide*,

$$CHMe_2\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2,$$

crystallises in prismatic needles, m. p. 134°; the corresponding *a-bromo*iso*hexoylglycinamide*,

$$CHMe_2\cdot CH_2\cdot CHBr\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2,$$

crystallises in microscopic needles, m. p. 100—102°. Aqueous ammonia has scarcely any action on a-bromo*iso*valerylglycinamide, but when it is heated with alcoholic ammonia at about 120° in a sealed tube, interaction occurs, and the product can be separated into two parts, one of which is scarcely soluble, whilst the other is readily soluble in water. The former consists of *valylglycine anhydride* (*diketo*iso*propylpiperazine*), $CH_2<\begin{matrix}NH\cdot CO\\ CO\cdot NH\end{matrix}>CH\cdot CHMe_2$, needles from hot water, m. p. 245°, whilst the latter is the *hydrobromide* of *valylglycinamide*, $CHMe_2\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2,HBr$, microscopic needles from alcohol-ether, m. p. 223°. By the action of aqueous ammonia at 40° on a-bromo*iso*hexoylglycinamide, a 20% yield of leucylglycine anhydride, diketo*iso*butylpiperazine, is obtained (compare Fischer and Brunner, A., 1905, i, 690).

Chloroacetylglycinamide, which has been previously described (A., 1910, i, 304), can be more readily obtained by the interaction of the components in aqueous than in ethereal solution, and the product, on treatment with aqueous ammonia, is readily converted into diketopiperazine, together with traces of *glycylglycinamide*, m. p. 195—196°, which, however, was not obtained in a pure state.

The *hydrochloride* of the previously described iminodiacetamide (compare Jongkees, A., 1908, i, 959) is readily prepared by the action of free glycinamide, or, better, glycinamide carbonate in aqueous solution on chloroacetamide. It crystallises from dilute alcohol in rosettes, m. p. 234—236°. *Benzoyliminodiacetamide*, $COPh\cdot N(CH_2\cdot CO\cdot NH_2)_2$, crystallises in microscopic needles, m. p. 225—227°. Iminodiacetamide reacts with bromo*iso*hexoyl bromide, forming *a-bromo*iso*hexoyliminodiacetamide*,

$$CHMe_2\cdot CH_2\cdot CHBr\cdot CO\cdot N(CH_2\cdot CO\cdot NH_2)_2,$$

which melts at 108—110°. It is very slowly acted on by aqueous ammonia. H. W. B.

Action of Hydrazine and Azines on Chloral and Bromal Hydrates. GUSTAV KNÖPFER (*Monatsh.*, 1916, **37**, 357—367. Compare A., 1913, i, 703).—Hydrazine salts and benzaldazine react with

molten bromal hydrate just as they do with chloral hydrate, giving compounds which contain 2 atoms of hydrogen less, per molecule, than the normal condensation products. The *compound*,

$$C_4H_2ON_2Br_6\ (2CBr_3{\cdot}CHO + N_2H_4 - H_2O - 2H),$$

forms white needles, m. p. 187°, and reacts violently with concentrated potassium hydroxide, but gently with dilute alkalis without the liberation of bromoform. The *compound*,

$$C_9H_7ON_2Br_3\ [CBr_3{\cdot}CH(OH)_2 + N_2(CHPh)_2 - C_6H_5{\cdot}CHO - 2H],$$

crystallises in silvery scales, m. p. 180°, dissolves in cold, dilute potassium hydroxide, but on warming with this agent deposits the *compound*, $C_9H_6ON_2Br_2$, in large tablets, m. p. 98°.

Experiments were conducted in order to find whether the same reactions occurred if the reagents were diluted by any solvent. Chloral hydrate was found to react in just the same way when diluted with glacial acetic acid, but bromal hydrate gave substances which differed by 1HBr, and not by 2H, from the normal condensation products. The *compound*,

$$C_4H_3ON_2Br_5\ (2CBr_3{\cdot}CHO + N_2H_4 - H_2O - HBr),$$

has m. p. 174°, and the *compound*, $C_9H_8ON_2Br_2$, has m. p. 213°, and differs from the above compound, $C_9H_6ON_2Br_2$, in being soluble in dilute potassium hydroxide.

Bromal hydrate reacts with hydrazine and semicarbazide in aqueous solutions to give the normal additive products; *bromalhydrazine*, $CBr_3{\cdot}CH(OH){\cdot}NH{\cdot}NH_2$, has m. p. 75°, and *bromalsemicarbazide*, $C_3H_6O_2N_3Br_3$, crystallises in needles, m. p. 87° (decomp.). J. C. W.

Halogenation. XI. Chlorination with Aqua Regia. Chlorination of Hydrocarbons. Rasik Lal Datta and Francis Vito Fernandes (*J. Amer. Chem. Soc.*, 1916, **38**, 1809—1813).—In continuation of the work on the chlorination of hydrocarbons by means of aqua regia (A., 1914, i, 675), it has been found that the xylenes, ethylbenzene, and dibenzyl give good results, but that the higher hydrocarbons either yield a complex product which cannot be separated into its constituents or suffer decomposition with formation of chloropicrin.

m-Xylene, when heated with a mixture of concentrated hydrochloric acid (2 parts) and nitric acid (1 part), yields liquid mono- and 4:6-di-chloro-derivatives and crystalline tri- and tetra-chloro-derivatives; the method is especially applicable to the preparation of 2:4:5:6-tetrachloro-*m*-xylene, m. p. 210°. *o*-Xylene, under similar conditions, gives mono- and di-chloro-derivatives and 3:4:5:6-tetrachloro-*o*-xylene, m. p. 215°. In the case of *p*-xylene, the chloro-derivatives produced are chloro-*p*-xylene, 2:5-dichloro-*p*-xylene, and tetrachloro-*p*-xylene, m. p. 217·5°. Ethylbenzene is converted by aqua regia into chloroethylbenzene, $CH_2Ph{\cdot}CH_2Cl$, and a crystalline substance, m. p. 171·5°, which has not been identified. Dibenzyl yields *p*-dichlorodibenzyl, m. p. 111°.

By the chlorination of 5-butyl-*m*-xylene, a yellow oil was obtained which had the odour of chloropicrin, and from which no pure chloro-derivatives could be isolated. Experiments were also

made with anthracene, phenanthrene, triphenylmethane, diphenylmethane, fluorene, naphthalene, cymene, styrene, and tetrahydronaphthalene, but pure chloro-derivatives could not be separated in any case. E. G.

Thermal Decomposition of the Aliphatic Hydrocarbon Derivatives of Naphthalene. G. EGLOFF (*J. Soc. Chem. Ind.*, 1916, **35**, 920; from *Met. Chem. Eng.*, 1916, **15**, 125—127).—The 'cracking' of an oil consisting mainly of alkyl and alkylene derivatives of naphthalene was effected by passing it at a definite rate through an electrically heated tube at 600—700° under pressures varying from 1 to 14 atm. The oil was obtained by the purification of a tar oil, from which naphthalene and anthracene had been extracted by refrigeration, and it gave on distillation 6·3, 75·0, 15·0, and 3·1% by volume of fractions boiling at 150—200°, 200—250°, 250—300°, and 300—325°, having $D^{15\cdot5}=0\cdot958$, 0·995, 0·999, and 0·998 respectively. The yield of benzene and toluene in the cracked oil increased with the temperature; at 650° and 14 atm. 3·2% by volume of benzene, calculated on the original oil, was produced, whilst the formation of toluene reached a maximum of 2% by volume at 600° and 14 atm., and 650° and 11 atm., further increase in temperature or pressure above these limits resulting in a decreased yield of toluene, and increased carbonisation. The formation of benzene and toluene is assumed to take place by the direct decomposition of methylnaphthalenes, the formation and subsequent decomposition of xylenes, and by synthesis from acetylene and allylene. G. F. M.

Preparation of Aromatic Amines. BADISCHE ANILIN & SODA-FABRIK (Eng. Pat., 5692, 1915; from *J. Soc. Chem. Ind.*, 1916, **35**, 920).—The copper catalyst may be prepared by reducing, at a temperature below red-heat, copper oxide prepared by precipitation, and not pyrogenetically, as specified in the main patent (A., 1915, i, 796). Hot sodium hydroxide solution is added, for example, to a solution of 1180 grams of copper nitrate, 38 grams of silver nitrate, and 252 grams of magnesium nitrate; the precipitate is washed, and 20 grams of it are mixed with 130 grams of pumice, a small amount of water, and 20 grams of 40% sodium silicate solution are added, and the pasty mass is reduced at 200° in a current of hydrogen. With this catalyst, nitrobenzene is reduced to aniline by hydrogen at 200—210°. G. F. M.

Preparation of Aniline, other Aromatic Amines, or other Substances Involving Catalytic Hydrogenation. BADISCHE ANILIN & SODA-FABRIK (Eng. Pat., 6409, 1915; from *J. Soc. Chem. Ind.*, 1916, **35**, 920).—Catalytic hydrogenation may be effected by employing carbon monoxide, or gases containing carbon monoxide, together with water vapour, in the proportion of at least one volume of the latter to three of the former. The reducing gases, mixed with the vapour of the nitro-compound, are passed over a contact mass containing copper at comparatively low tem-

peratures (200—220° for nitrobenzene). The contact may be prepared by coating 130 grams of pumice stone with a mixture of 24·3 grams of cupric carbonate, 2·7 grams of zinc carbonate, and 20 grams of sodium silicate solution, and reducing at a low temperature. G. F. M.

Thiocyanates and Thiocarbimides. X. Utilisation of Tetrachloromethyl Mercaptan for the Preparation of Alkyl Thiocarbimides. TREAT B. JOHNSON and E. HEATON HEMINGWAY (*J. Amer. Chem. Soc.*, 1916, **38**, 1860—1867).—It has been shown by Rathke that tetrachloromethyl mercaptan reacts with amines to form thiolamines of the type $NHR{\cdot}S{\cdot}CCl_3$. He prepared the thiolaniline, $NHPh{\cdot}S{\cdot}CCl_3$, and the corresponding thiol-*o*- and -*p*-toluidines, and found that when these compounds are treated with alcoholic potassium hydroxide they are converted into unstable substances, the structure of which has not hitherto been established. Rathke also stated that when the thiolanilines are heated they undergo decomposition with formation of volatile products and sulphur compounds with the odour of thiocarbimides. The present work was undertaken for the purpose of studying the latter reaction.

The three compounds described by Rathke were prepared. Trichloromethylthiolaniline and trichloromethylthiol-*o*-toluidine were obtained as oils, whilst the thiol-*p*-toluidine was obtained in the form of colourless crystals, m. p. 72°. By the action of alcoholic potassium hydroxide on trichloromethylthiolaniline, cyclic dichloromethylenephenyliminosulphide, $NPh{<}\overset{S}{\underset{CCl_2}{|}}$, m. p. 140°, was obtained, which crystallises in prisms. The corresponding *p*-tolyliminosulphide decomposes violently at 145°, and the *o*-tolyliminosulphide has m. p. 112°.

When trichloromethylthiolaniline is heated at 125—130° it suffers decomposition with formation of phenylthiocarbimide, hydrogen chloride, and a brown *compound*, which possibly has the structure $\overset{S}{\underset{PhN}{|}}{>}C{:}C{<}\overset{S}{\underset{NPh}{|}}$. Similarly, trichloromethylthiol-*o*-toluidine yields *o*-tolylthiocarbimide, and trichloromethylthiol-*p*-toluidine furnishes *p*-tolylthiocarbimide and a brown *solid*, probably

$$C_6H_4Me{\cdot}\overset{S}{\underset{N}{|}}{>}C{:}C{<}\overset{S}{\underset{N}{|}}{\cdot}C_6H_4Me.$$

When cyclic dichloromethylene-*p*-tolyliminosulphide is heated it undergoes decomposition with formation of *p*-tolylthiocarbimide and a brown compound, probably identical with that obtained by the action of heat on trichloromethylthiol-*p*-toluidine. E. G.

Catalytic Decomposition of Certain Phenol Silver Salts. I. W. H. HUNTER, A. O. OLSON, and E. A. DANIELS (*J. Amer. Chem. Soc.*, 1916, **38**, 1761—1771).—Torrey and Hunter, during the course of work on the red and white silver salts of 2 : 4 : 6-tribromophenol (A., 1911, i, 283), observed that these salts react with ethyl

iodide with formation of a white, amorphous compound. A study has now been made of the composition of this substance, the preparation of analogous compounds, and the nature of the reaction by which they are formed.

The white, amorphous *compound*, $(C_6H_2OBr_2)_n$, from the silver salt of tribromophenol, sinters above 260° and becomes nearly black at 290°; it is proposed provisionally to term this compound "*polydibromophenylene oxide*." The silver salt of tribromoresorcinol methyl ether behaves similarly with alkyl iodides, yielding the amorphous *compound*, $(OMe{\cdot}C_6HOBr_2)_n$. The silver salt of trichlorophenol, however, when treated with ethyl iodide, yields very little amorphous compound, but is converted into trichlorophenetole.

The formation of these amorphous compounds takes place in the sense of the equation $nC_6H_2Br_3{\cdot}OAg = nAgBr + (C_6H_2OBr_2)_n$. The change occurs on suspending the silver salt in alkyl iodides or in benzene, and is also effected by heating the salt at slightly more than 100°. It is suggested that this peculiar decomposition may be due to a stress existing in the molecule of the silver salt between the silver atom and the halogen atom which separates with it, this stress not being sufficient to cause decomposition until some catalytic effect is exerted on the molecule by heat or by the liquid brought into contact with it.

When the silver salt of tribromoresorcinol methyl ether is treated with ethyl iodide there is formed, in addition to the amorphous compound, *tribromoresorcinol methyl ethyl ether*,

$$OMe{\cdot}C_6HBr_3{\cdot}OEt,$$

m. p. 75°. E. G.

Some Dihydroxynaphthalenes. OTTO FISCHER (*J. pr. Chem.*, 1916, [ii], **94**, 1—48. Compare Fischer and König, A., 1914, i, 712).—An examination of some of the derivatives of 1:6- and 2:7-dihydroxynaphthalene.

I. [With CONSTANZE BAUER.]—The following compounds were prepared from 1:6-dihydroxynaphthalene. *Dibenzoyl* derivative, colourless prisms, m. p. 103—104°. 1:6-*Dimethoxynaphthalene*, $C_{12}H_{12}O_2$, obtained by the action of methyl sulphate and potassium hydroxide solution, colourless needles, m. p. 60—61°. 1:6-*Diethoxynaphthalene*, $C_{14}H_{16}O_2$, prepared in a similar manner to the last, colourless needles, m. p. 83°. Treatment of 1:6-dihydroxynaphthalene in cold acetic acid solution with sodium nitrite gave rise to 2-*nitroso*-1:6-*dihydroxynaphthalene*, $C_{10}H_7O_3N$, red leaflets, decomp. 180—230° (*diacetyl* derivative, yellow prisms, decomp. near 154°), together with a smaller quantity of 4-*nitroso*-1:6-*dihydroxynaphthalene*, yellow needles, decomp. 200—220° (*diacetyl* derivative, almost colourless needles, decomp. near 156°), the former being much less soluble in alcohol.

Reduction of 2-nitroso-1:6-dihydroxynaphthalene with stannous chloride and hydrochloric acid produces 2-*amino*-1:6-*dihydroxynaphthalene*, an unstable substance (*hydrochloride*, $C_{10}H_{10}O_2NCl$, prisms; *triacetyl* derivative, lustrous needles, m. p. 150°). The

hydrochloride of this base, when treated in aqueous solution with a concentrated solution of ammonia, yields a green solution which becomes blue on shaking in the air, this result being characteristic of 2-amino-1-hydroxynaphthalene derivatives. Further confirmatory evidence as to the structure of the nitroso-compound is forthcoming from its deep colour and its resistance to the action of ammonia, even under pressure at 100°.

When reduced with stannous chloride and hydrochloric acid, 4-nitroso-1:6-dihydroxynaphthalene is converted into 4-*amino*-1:6-*dihydroxynaphthalene*, an easily oxidisable substance (*stannichloride*, sparingly soluble), which on addition to dilute ferric chloride solution yields 6-*hydroxy*-1:4-*naphthaquinone*, $C_{10}H_6O_3$, reddish-yellow needles, m. p. 170° (decomp.); this is reducible by stannous chloride and hydrochloric acid to 1:4:6-*trihydroxynaphthalene*, $C_{10}H_8O_3$, colourless needles, m. p. 138—140° (*triacetyl* derivative, colourless needles, m. p. 94—95°), which readily undergoes reoxidation to the quinone.

In the action of diazonium salts on 1:6-dihydroxynaphthalene the number of azo-groups entering depends on the experimental conditions. In acid solution the dihydroxy-compound couples with a benzenediazonium salt, yielding almost entirely 4-*benzeneazo*-1:6-*dihydroxynaphthalene*, $C_{16}H_{12}O_2N_2$, red needles, m. p. near 230° (decomp.); in cold aqueous pyridine the reaction product is almost exclusively *bisbenzeneazo*-1:6-*dihydroxynaphthalene*,

$$C_{22}H_{16}O_2N_4,$$

needles with a green, metallic lustre; in strongly alkaline solution, either with excess of alkali hydroxide or in pyridine solution with the addition of alkali hydroxide, *tris-benzeneazo*-1:6-*dihydroxynaphthalene*, $C_{28}H_{20}O_2N_6$, needles or prisms with metallic lustre, is obtained in good yield.

II. [With Constanze Bauer.]—1:5-Dihydroxynaphthalene (*dichlorodiacetyl* derivative, $C_{14}H_{10}O_4Cl_2$, colourless needles; *dibenzoyl*-derivative, colourless needles, m. p. 235°) was converted into 1:5-dimethoxynaphthalene, $C_{12}H_{12}O_2$, m. p. 181—182°, and 1:5-*diethoxynaphthalene*, $C_{14}H_{16}O_2$, colourless leaflets, m. p. 130°, the former compound reacting with bromine in benzene solution with formation of a *bromodimethoxynaphthalene*, $C_{12}H_{11}O_2Br$, colourless leaflets, m. p. 115°. By the action of methyl sulphate and potassium hydroxide on dihydroxynaphthalene there can also be produced 5-methoxy-α-naphthol, m. p. 140° (*acetyl* derivative, colourless crystals, m. p. 68°; *chloroacetyl* derivative, colourless needles, m. p. 85°; *benzoyl* derivative, silvery, lustrous needles, m. p. 102°), which in acetic acid solution reacts with sodium nitrite, giving 2-*nitroso*-5-*methoxy*-α-*naphthol* (5-*methoxy*-1:2-*naphthaquinonemonoxime*), $C_{11}H_9O_3N$, deep yellow needles, m. p. 165° (decomp.). This, by the gradual addition of phenylhydrazine to its boiling benzene solution, was converted into 2-*amino*-5-*methoxy*-α-*naphthol*, $C_{11}H_{11}O_2N$, silvery leaflets, m. p. 158° (decomp.), and in aqueous methyl-alcoholic solution condensed with hydroxylamine hydrochloride, yielding 5-*methoxy*-1:2-*naphthaquinonedioxime*,

$$C_{11}H_{10}O_3N_2,$$

golden-yellow needles, decomp. at 195°, together with the corresponding anhydride, 5-*methoxy*-1:2-*naphthafurazan*, $C_{11}H_8O_2N_2$, yellow needles, m. p. 159°.

5-Methoxy-1-naphthol in alkaline solution condenses with benzenediazonium chloride, producing 4-*benzeneazo*-5-*methoxy-α-naphthol*, $C_{17}H_{14}O_2N_2$, red needles with a green glance, m. p. 155° (decomp.; *acetyl* derivative, yellowish-brown, crystalline aggregates, m. p. 123°), whilst in more strongly alkaline solution and with a bimolecular proportion of the benzenediazonium salt, 2:4-*bisbenzeneazo*-5-*methoxy-α-naphthol*, $C_{23}H_{18}O_2N_4$, bronze-coloured needles, m. p. 204° (decomp.), insoluble in alkali, is formed.

1:5-Dihydroxynaphthalene, when treated under varying conditions in acetic acid solution with a unimolecular or bimolecular proportion of nitrous acid, yields only one nitroso-derivative, which from its colour and by analogy with the action of nitrous acid on the corresponding monomethyl ether must be 2-*nitroso*-1:5-*dihydroxynaphthalene*, $C_{10}H_7O_3N$, reddish-brown needles, decomp. near 190°. In coupling with diazonium salts, 1:5-dihydroxynaphthalene shows a marked tendency to form only a mono-azo-derivative; the method generally followed was to allow the compound to react with the diazo-solution in alkaline solution with or without the addition of pyridine, and there were thus obtained 4-*benzeneazo*-1:5-*dihydroxynaphthalene*, $C_{16}H_{12}O_2N_2$, red needles, m. p. 210° (decomp.), and 4-p-*nitrobenzeneazo*-1:5-*dihydroxynaphthalene*, $C_{16}H_{11}O_4N_3$, red crystals with a green glance, m. p. near 250° (decomp.). By using a strongly alkaline solution and a large excess of diazonium salt it was, however, found possible to prepare a *bisbenzeneazo*-1:5-*dihydroxynaphthalene*, $C_{22}H_{16}O_2N_4$, needles with a metallic lustre, m. p. above 250°.

III. [With Fr. Hammerschmidt.]—2-Hydroxy-7-methoxynaphthalene, m. p. 117° (Bünzly and Decker, A., 1905, i, 884, give 113—114°), gives an *acetyl* derivative, colourless needles, m. p. 130°, *benzoyl* derivative, colourless leaflets, m. p. 140°, and *chloroacetyl* derivative, colourless leaflets, m. p. 106°. In acetic acid solution it reacts with sodium nitrite, yielding 1-*nitroso*-2-*hydroxy*-7-*methoxynaphthalene* (7-*methoxy*-1:2-*naphthaquinonemonoxime*), $C_{11}H_9O_3N$, red or bronze needles or leaflets, m. p. 129°, which in boiling aqueous methyl-alcoholic solution condenses with hydroxylamine hydrochloride, producing 7-*methoxy*-1:2-*naphthaquinonedioxime*, $C_{11}H_{10}O_3N_2$, yellow needles, m. p. 150°, and its *anhydride*, $C_{11}H_8O_2N_2$, almost colourless needles, m. p. 129°. On reduction with phenylhydrazine in benzene solution, 1-nitroso-2-hydroxy-7-methoxynaphthalene is converted into 1-*amino*-2-*hydroxy*-7-*methoxynaphthalene*, $C_{11}H_{11}O_2N$, almost colourless leaflets, m. p. 170°. Treatment with concentrated ammonia under pressure at 100° converts the nitroso-compound into 1-*nitroso*-2-*amino*-7-*methoxynaphthalene*, $C_{11}H_{10}O_2N_2$, yellowish-brown needles, m. p. 194° (*hydrochloride*, red prisms, m. p. 234°; *picrate*, red crystals, m. p. 207°), which on reaction with hydroxylamine gives the already described 7-methoxy-1:2-naphthaquinonedioxime. In a similar manner the

nitroso-compound reacts with a solution of methylamine, forming 1-*nitroso*-2-*methylamino*-7-*methoxynaphthalene*, $C_{12}H_{12}O_2N_2$, green leaflets, m. p. 136° (*hydrochloride*, reddish-brown needles, m. p. 144°; *picrate*, deep red prisms, m. p. 164°; *nitrosoamine*, $C_{12}H_{11}O_3N_3$, almost colourless needles, m. p. 158°), whilst with ethylamine it yields 1-*nitroso*-2-*ethylamino*-7-*methoxynaphthalene*, $C_{13}H_{14}O_2N_2,H_2O$, deep brown prisms, m. p. 60—72°, or, when anhydrous, deep green crystals, m. p. 89°; *hydrochloride*, red, stellar aggregates, m. p. 101°; *picrate*, deep red needles, m. p. 270°.

It is already known that 1-nitroso-2-ethylaminonaphthalene under the influence of alcoholic hydrochloric acid eliminates water with formation of ethenyl-1:2-naphthylenediamine [2-methyl-1:2-naphthiminazole] (Fischer and Hepp, A., 1887, 1114), and it is now found that 1-nitroso-2-methylamino-7-methoxynaphthalene can undergo a similar change, but the result is more conveniently achieved by warming in acetic acid with zinc chloride; the product is 8-*methoxy*-1:2-*naphthiminazole*, $C_{12}H_{10}ON_2$, m. p. 224°; *hydrochloride*, needles, m. p. 255°; *aurichloride*, yellow crystals, m. p. 211°; *platinichloride*, reddish-yellow, crystalline powder, m. p. 270° (decomp.). On demethylation with hydrochloric acid at 170—180°, this substance gives 8-*hydroxy*-1:2-*naphthiminazole*, $C_{11}H_8ON_2$, colourless needles, m. p. 274°. In an analogous manner to the methyl compound, 1-nitroso-2-ethylamino-7-methoxynaphthalene can be easily dehydrated, the product in this case being 8-methoxy-2-methyl-1:2-naphthiminazole.

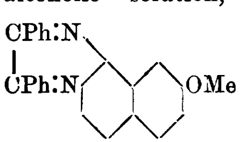
It was found possible to couple 2-hydroxy-7-methoxynaphthalene with only one diazonium nucleus, interaction with benzenediazonium chloride under various conditions yielding 1-*benzeneazo*-2-*hydroxy*-7-*methoxynaphthalene*, $C_{17}H_{14}O_2N_2$, red needles, m. p. 121°, insoluble in alkali. 1-p-*Nitrobenzeneazo*-2-*hydroxy*-7-*methoxynaphthalene*, $C_{17}H_{13}O_4N_3$, obtained in a similar manner, but with the use of *p*-nitrobenzenediazonium chloride, forms deep red needles, m. p. 238°, insoluble in alkali.

IV. [With WILH. KERN.]—1-*Nitro*-2:7-*dimethoxynaphthalene*, $C_{12}H_{11}O_4N$, yellow prisms or tablets, m. p. 141°, prepared by treating the dimethoxynaphthalene (Bünzly and Decker, *loc. cit.*) with nitric acid in the presence of acetic acid, is reducible by stannous chloride and hydrochloric acid to 1-*amino*-2:7-*dimethoxynaphthalene*, $C_{12}H_{13}O_2N$, colourless, silky needles, m. p. 82—83°; *hydrochloride*, needles or leaflets; *picrate*, yellow needles, m. p. 152°; *acetyl* derivative, colourless leaflets, m. p. 179—180°; *benzoyl* derivative, short needles, m. p. 182°. When heated with alcoholic ammonia solution at 190—200°, 1-nitro-2:7-dimethoxynaphthalene loses a methoxy-group with formation of 1-*nitro*-2-*amino*-7-*methoxynaphthalene*, $C_{11}H_{10}O_3N_2$, reddish-yellow needles, m. p. 115—116°; *hydrobromide*, yellow leaflets, m. p. 159—160° (decomp.); *picrate*, red needles, m. p. 125°; *acetyl* derivative, yellow needles, m. p. 149—150°; *benzoyl* derivative, pale yellow, silky needles, m. p. 203—204°; *benzylidene* derivative, red aggregates, m. p. 126—127°; *salicylidene* derivative, brown needles, m. p. 202°. If the nitrodimethoxynaphthalene is heated with alcoholic methylamine solu-

tion at 160—165° there is obtained 1-*nitro*-2-*methylamino*-7-*methoxynaphthalene*, $C_{12}H_{12}O_3N_2$, yellowish-red needles, m. p. 149—150°.

When heated with nitric acid at 100° until it has entirely passed into solution, 1-nitro-2 : 7-dimethoxynaphthalene is converted into *trinitro*-2 : 7-*dimethoxynaphthalene*, $C_{12}H_9O_8N_3$, pale yellow needles, m. p. 216°, together with a little 3-*nitro*-4-*methoxyphthalic acid*, $C_9H_7O_7N$, colourless needles, m. p. 212°.

Reduction with tin and hydrochloric acid converts 1-nitro-2-amino-7-methoxynaphthalene into 1 : 2-*diamino*-7-*methoxynaphthalene*, unstable, colourless needles, m. p. 188°, the *hydrochloride*, $C_{11}H_{14}ON_2Cl_2$, m. p. 234—235°, of which condenses with benzil in alcoholic solution, giving 9-*methoxy*-2 : 3-*diphenylnaphthaquinoxaline* (annexed formula), pale yellow needles, m. p. 168°. In an analogous manner condensation with phenanthraquinone yields 7′-*methoxy*-1′ : 2′-*naphthaphenanthradiazine*, $C_{25}H_{16}ON_2$, pale brown needles, m. p. 271—272°.



On treatment in acetic acid solution with nitric acid (D 1·52) at the ordinary temperature, 2 : 7-dimethoxynaphthalene is converted into 1 : 8-*dinitro*-2 : 7-*dimethoxynaphthalene*, $C_{12}H_{10}O_6N_2$, yellow prisms or needles, m. p. 286°, which is reducible by stannous chloride and hydrochloric acid with production of 1 : 8-*diamino*-2 : 7-*dimethoxynaphthalene*, colourless needles or prisms, m. p. 115°; *dihydrochloride*, $C_{12}H_{16}O_2N_2Cl_2$; *sulphate*, sparingly soluble; *picrate*, yellow needles; *mercurichloride*, sparingly soluble in cold water. The dinitro-compound reacts with alcoholic ammonia at 190—200°, eliminating its methoxy-groups with formation of 1 : 8-*dinitro*-2 : 7-*diaminonaphthalene*, $C_{10}H_8O_4N_4$, red prisms, m. p. 265—266°; *picrate*, $C_{22}H_{14}O_{18}N_{10}$, yellow crystals, m. p. 180—181°; *diacetyl* derivative, golden-yellow leaflets, m. p. 278°; *dibenzoyl* derivative, yellow needles, m. p. 205°. With an alcoholic methylamine solution at 160—165°, the dinitrodimethoxynaphthalene reacts in an analogous manner, giving 1 : 8-*dinitro*-2 : 7-*dimethyldiaminonaphthalene*, $C_{12}H_{12}O_4N_4$, red needles, m. p. 274°. D. F. T.

Deoxyhydrocatechin Tetramethyl Ether. HUGH RYAN and MICHAEL J. WALSH (*Sci. Proc. Roy. Dublin Soc.*, 1916, **15**, 113—120).—In order to render possible a decision between the rival chroman and coumaran structures for catechin (Perkin and Yoshitake, T., 1902, **81**, 1169; von Kostanecki and Lampe, A., 1907, i, 73), the authors have attempted the synthesis of 2 : 4 : 6 : 3′ : 4′-pentamethoxy-3-ethyldiphenylmethane; this, according to the coumaran structure for catechin, should be identical with the deoxyhydrocatechin pentamethyl ether, m. p. 83—84°, which was obtained by methylation of the oily deoxyhydrocatechin tetramethyl ether, the latter being the product of the energetic reduction of catechin tetramethyl ether (von Kostanecki and Lampe, A., 1907, i, 335).

Phloroglucinol trimethyl ether was converted into phloraceto-

phenone trimethyl ether, $C_6H_2Ac(OMe)_3$, which on reduction with amalgamated zinc and hydrochloric acid yielded *ethylphloroglucinol trimethyl ether*, $C_6H_2Et(OMe)_3$, m. p. 29—30°. On condensation with veratroyl chloride in carbon disulphide in the presence of aluminium chloride, this substance was converted into *veratroylethylphloroglucinol trimethyl ether*,

$$C_6H_3(OMe)_2{\cdot}CO{\cdot}C_6HEt(OMe)_3,$$

colourless plates, m. p. 123—124°. Unfortunately, the reduction product of this substance, namely, 2 : 4 : 6 : 3′ : 4′-*pentamethoxy*-3-*ethyldiphenylmethane*, whether prepared by treatment with sodium and alcohol or with amalgamated zinc and hydrochloric acid, was obtained only as an oil which resisted all attempts to induce crystallisation even when inoculated with a crystal of deoxyhydrocatechin pentamethyl ether. The result therefore permits no definite conclusion to be drawn. D. F. T.

Existence of Trisulphur Chloride, S_3Cl_2. M. M. Richter (*Ber.*, 1916, **49**, 1024—1025).—Inorganic sulphur chlorides often behave as if they consisted of a mixture of two chlorides. For example, thionyl chloride under certain conditions reacts as if it were a mixture of sulphur chloride (SCl_2) and sulphuryl chloride (compare Michaelis, A., 1890, 610). The author has observed a similar behaviour with disulphur chloride, which reacts towards *p*-chlorophenol as if it were a mixture of sulphur chloride and trisulphur chloride, in accordance with the equation, $2S_2Cl_2 = SCl_2 + S_3Cl_2$, giving a mixture of 5 : 5′-dichloro-2 : 2′-dihydroxydiphenyl sulphide and the corresponding trisulphide. If sulphur is added to the reaction mixture, the yield of trisulphide is increased.

5 : 5′-Dichloro-2 : 2′-dihydroxydiphenyl sulphide, $[C_6H_3(OH)Cl]_2S$ (compare Gazdar and Smiles, T., 1911, **97**, 2252), is obtained when *p*-chlorophenol (12·85 grams) is heated with excess of disulphur chloride (7·5 grams) in carbon disulphide solution (100 c.c.). After twenty-four hours the resulting mass of crystals is collected and recrystallised from benzene, when the sulphide is obtained as glistening needles, m. p. 174°. A better yield is obtained when sulphur chloride is used instead of disulphur chloride. The *dimethyl ether*, $C_{14}H_{12}O_2Cl_2S$, forms badly defined, stout crystals, m. p. 112°, whilst the *dibenzoate*, $C_{26}H_{16}O_4Cl_2S$, crystallises in needles, m. p. 145°.

The mother liquor remaining after the sulphide crystals have been collected deposits, on keeping, badly defined crystals of 5 : 5′-*dichloro*-2 : 2′-*dihydroxydiphenyl trisulphide*, $[C_6H_3(OH)Cl]_2S_3$, m. p. 133°. The same substance is obtained in a purer condition and in larger quantity when sulphur (1·6 grams) is added to the reaction mixture of *p*-chlorophenol (12·85 grams) and disulphur chloride (6·75 grams); the reaction commences only after heating at 40° for some time. The *dibenzoate*, $C_{26}H_{16}O_4Cl_2S_3$, gives micro-crystals, m. p. 145°. T. S. P.

β-Naphthol Sulphide and *iso*-β-Naphthol Sulphide. III. O. Hinsberg (*J. pr. Chem.*, 1916, [ii], **93**, 277—301. Compare A., 1915, i, 237, 808).—β-Naphthol sulphide is almost unaffected by

boiling with 10% sodium hydroxide for ten hours, only a small portion being decomposed into sulphur and β-naphthol. A benzene solution of the sulphide, heated for two hours at 210°, yields unchanged sulphide, a yellow resin, and a small quantity of β-naphthol disulphide.

A warm alcoholic solution of *iso*-β-naphthol sulphide treated with concentrated aqueous silver nitrate and sodium acetate yields a *silver* salt, $2C_{20}H_{12}O_2SAg_2,C_{20}H_{14}O_2S$, grey, crystalline powder, from which a mixture of the *dimethyl ether* and the *monomethyl ether*, $C_{21}H_{16}O_2S$, pale yellow prisms, m. p. 134°, is obtained by means of methyl iodide and methyl alcohol. The latter ether alone is obtained from the *zinc* salt, $(C_{20}H_{13}O_2S)_2Zn$, colourless, crystalline powder.

β-Naphtholsulphone, m. p. 235°, not 225°, as stated previously, is converted partly into β-naphthol, sulphuric acid, and an amorphous substance by water at 180° or by a mixture of glacial acetic and concentrated hydrochloric acids at the same temperature. Its sodium salt, when heated with water at 200°, yields sodium sulphite and 2-hydroxy-α-naphthyl β-naphthyl ether; the same products are also obtained from the sodium salt of *iso*-β-naphtholsulphone.

When heated at 200° with acetic anhydride and sodium acetate, β-naphtholsulphone diacetate is converted into naphthathioxin dioxide (Nolan and Smiles, T., 1913, **103**, 901); with chloroform and phosphoryl chloride at 160—170° the sulphone yields a mixture, yellow crystals, m. p. 220—240°, apparently of chlorinated naphthathioxins.

β-Naphtholsulphone diacetate, $SO_2(C_{10}H_6\cdot OAc)_2$, glassy prisms, m. p. 220°, is obtained by oxidising the corresponding sulphide with glacial acetic acid and 30% hydrogen peroxide on the water-bath.

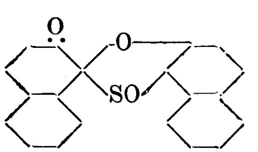
β-Naphtholsulphone forms a *dimethyl* ether, $SO_2(C_{10}H_6\cdot OMe)_2$, colourless crystals, which has m. p. 205° (decomp.) when heated moderately rapidly in a tube, but decomposes at 150° in a platinum crucible: it is converted into sulphuric acid and β-naphthyl methyl ether when boiled with glacial acetic acid containing a little concentrated sulphuric acid.

The substance $C_{20}H_{14}O_2$, m. p. 197°, obtained by reducing dehydro-β-naphtholsulphone with zinc dust and glacial acetic acid containing a little hydrochloric acid, is not a dinaphthol as previously stated (A., 1915, i, 808); it contains only one hydroxyl group, and is very probably 2-hydroxy-α-naphthyl β-naphthyl ether.

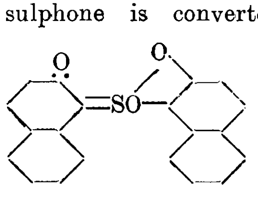
iso-β-Naphtholsulphone is not attacked by boiling aqueous sodium carbonate or 10% sodium hydroxide. When kept for several weeks in a desiccator over sulphuric acid or in a sealed tube, it undergoes a partial change into the anhydride, $C_{20}H_{12}O_3S$, and ultimately into 2-hydroxy-α-naphthyl β-naphthyl ether. The *monomethyl ether*, $OMe\cdot C_{10}H_6\cdot SO_2\cdot C_{10}H_6\cdot OH$, prisms, m. p. 218°, is obtained by oxidising the monomethyl ether of *iso*-β-naphthol sulphide with 30% hydrogen peroxide in hot glacial acetic acid, a by-product, colourless or faintly yellow crystals, m. p. 195°, being probably

iso-β-*naphtholsulphoxide monomethyl ether.* iso-β-*Naphtholsulphone dimethyl ether*, $SO_2(C_{10}H_6 \cdot OMe)_2$, can be prepared (1) in a similar manner from *iso*-β-naphthol sulphide dimethyl ether, (2) from the monomethyl ether, sodium methoxide, and methyl iodide, and (3) from *iso*-β-naphtholsulphone and methyl sulphate in the presence of alkali. It forms a crystalline powder, melts at 88° to a viscous liquid which becomes mobile at about 120°, and is remarkably stable, being unchanged by boiling dilute acids or alkalis or by zinc dust and acetic and hydrochloric acids. *iso*-β-Naphtholsulphone dissolved in dilute aqueous sodium carbonate is converted by benzenesulphonyl chloride into the *dibenzenesulphonyl* derivative, $SO_2(C_{10}H_6 \cdot O \cdot SO_2Ph)_2, H_2O$, m. p. 120°, faintly yellow needles from dilute acetic acid (it separates from glacial acetic acid in an amorphous condition), and into the *di*-p-*nitrobenzoyl* derivative, pale yellow crystals, m. p. 202°, by *p*-nitrobenzoyl chloride at 80°.

The anhydride, $C_{20}H_{12}O_3S$, obtained by heating *iso*-β-naphtholsulphone with glacial acetic acid on the water-bath (*loc. cit.*) (β-naphthaquinone has now been discovered as a by-product in this reaction) forms yellowish-brown needles, m. p. 95°, and is converted by boiling acetyl chloride into a yellow *substance*, m. p. about 120°, not into chlorinated *iso*naphthathioxins as previously stated (*loc. cit.*). The anhydride readily loses its sulphur atom by reduction in methyl-alcoholic solution with zinc dust and dilute hydrochloric acid, 2-hydroxy-α-naphthyl β-naphthyl ether being formed, and is therefore regarded as a sulphoxide of the annexed formula. It forms a p-*nitrophenylhydrazone*, brownish-red powder, not a di-*p*-nitrophenylhydrazone as stated (*loc. cit.*).



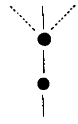
By careful treatment with a large excess of acetyl chloride at 10°, *iso*-β-naphtholsulphone is converted into a second *anhydride*, $C_{20}H_{12}O_3S$, brownish-red needles, m. p. 83°, to which the annexed formula is ascribed. It reacts easily with *p*-nitrophenylhydrazine, is reduced to *iso*-β-naphthol sulphide by zinc dust and glacial acetic acid, and is converted into mono- and di-chloro*iso*naphthathioxins by the continued action of acetyl chloride. C. S.



The Sulphur Atom. O. HINSBERG (*J. pr. Chem.*, 1916, [ii], **93**, 302—311).—An attempt is made to explain the isomerism of certain compounds containing sulphur, for example, the isomeric β-naphthol sulphides and sulphones (preceding abstract), *p*-acetylaminophenyl mercaptans, dithioacetanilides, and thiosalicylic acids, by ascribing spatial properties to the sulphur atom whereby an isomerism of this atom becomes conceivable. Thiophen may be regarded as benzene in which the group $\cdot CH{:}CH \cdot$ is replaced by $\cdot S \cdot$. If the C-pair is regarded as two contiguous spheres, then the

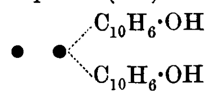
sulphur atom is represented by an ellipsoid, the long axis of which is approximately twice the diameter of a sphere. If two carbon atoms are represented by two tetrahedra joined at an apex, the sulphur atom becomes a triangular prism, the altitude of which equals that of the two tetrahedra. In either case the valency forces are assumed to emanate from two centres. The direction of the forces may be along the axis joining the two centres (I) or


(I.)


(II.)

the forces may originate from one centre only, their directions lying in a plane with the axis and making with the latter equal angles greater than 90° (II). β-Naphthol sulphide (III) is derived


(III.)


(IV.)

from (I), the formula, owing to the separation of the hydroxyl groups, accounting for the difficulty of converting this sulphide into its anhydride (naphthathioxin). *iso*-β-Naphthol sulphide, which is easily converted into the anhydride (Nolan and Smiles, T., 1913, **103**, 347), is represented by (IV), derived from the isomeric sulphur atom (II).

The conception is extended to quadri- and sexa-valent sulphur atoms. C. S.

Chromibenzoates. R. F. WEINLAND and HERMANN SPANAGEL (*Ber.*, 1916, **49**, 1003—1012).—Hitherto the investigations of Weinland and his co-workers on complex chromium salts have dealt only with the complexes formed with fatty acids (compare A., 1908, i, 935; 1909, i, 757; 1910, i, 296; 1912, i, 530). The present authors have extended the investigation to the complex chromium salts formed with benzoic acid, those previously prepared not having been very definitely characterised (Schiff, *Annalen*, 1862, **124**, 160; Calcagni, A., 1913, i, 1154).

A dilute solution of green chromium chloride (1 mol.), when treated with a solution of sodium benzoate (3 mols.), gives a violet precipitate of an insoluble *basic salt*, having a composition approximating to the formula $Cr_3(OBz)_{5\cdot5}(OH)_{3\cdot5},1\frac{1}{2}H_2O$. When the proportion of sodium benzoate varies from 1 to 2 mols. for each mol. of chromium chloride, a greyish-green precipitate is produced which, on extraction with alcohol, gives a green solution, leaving the above-mentioned insoluble, violet, basic salt behind. From the green alcoholic solution, on evaporation, a green, badly crystallised salt of indefinite composition is obtained, which can, however, be used for preparing pure salts. It contains chlorine, as well as chromium and benzoic acid residues; when the alcoholic solution is

digested with a quantity of silver benzoate equivalent to the chlorine present, and the silver chloride collected, it deposits green, rhombic crystals having a composition agreeing with that of *dihydroxyhexabenzoatotrichromi-benzoate*, $\left[Cr_3\begin{matrix}(OBz)_6\\(OH)_2\end{matrix}\right]OBz,2H_2O$. From the alcoholic solution of this salt, by appropriate treatment with hydrochloric acid, the corresponding *chloride*,

$$\left[Cr_3\begin{matrix}(OBz)_6\\(OH)_2\end{matrix}\right]Cl,3H_2O,$$

is obtained as long, rectangular, green plates. The same chloride can also be prepared by direct treatment with hydrochloric acid of the above-mentioned green salt of indefinite composition, or from the insoluble violet salt by heating it with hydrochloric acid under alcohol. When hydrochloric acid is replaced by nitric and perchloric acids respectively, the corresponding *nitrate*, $\left[Cr_3\begin{matrix}(OBz)_6\\(OH)_2\end{matrix}\right]NO_3,3H_2O$, and *perchlorate*,

$$\left[Cr_3\begin{matrix}(OBz)_6\\(OH)_2\end{matrix}\right]ClO_4,2H_2O,$$

are obtained in the form of green, rectangular plates.

The above salts are fairly stable, ammonium hydroxide precipitating chromium hydroxide from their alcoholic solutions only on prolonged heating.

No definite constitution could be assigned to the violet salt, which is insoluble in water or alcohol, although soluble in acetone or pyridine. T. S. P.

Solubility of Aminobenzoic Acid in Salt Solutions. HANS EULER (*Zeitsch. physiol. Chem.*, 1916, **97**, 291—292).—The author directs attention to the fact that the explanation of the increased solubility of anthranilic acid in neutral salt solutions given by Lundén (A., 1906, ii, 265) has been confirmed by Pfeiffer and Würgler (this vol., i, 713). H. W. B.

Internal Salts of Sexavalent Osmium and of Cobalt and Nickel, with Salicylic Acid. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 74—80. Compare A., 1915, i, 497, 538).—The complex salicylates of osmyl, cobalt, and nickel now described correspond with the general formula $\left[M<\left(\begin{matrix}O\cdot C_6H_4\\O\cdot CO\end{matrix}\right)_2\right]R_2$, representing the constitution of the cupro-, pallado-, and vanadyl-salicylates.

Potassium osmylsalicylate, $\left[O_2Os<\left(\begin{matrix}O\cdot C_6H_4\\O\cdot CO\end{matrix}\right)_2\right]K_2$, gradually separates in shining, reddish-brown, acicular crystals when an aqueous potassium salicylate solution is treated with potassium osmate and the liquid made neutral by addition of salicylic acid. It was analysed by passing a current of oxygen-free hydrogen and then a mixture of hydrogen and hydrogen chloride over the substance contained in a porcelain boat in a hard glass tube, and gradu-

ally heating the tube near the boat until all the salicylic acid is driven off, to be deposited in the cooler part of the tube. The latter is allowed to cool while carbon dioxide is passed through it, and the residual mixture of metallic osmium and potassium chloride in the boat extracted with water and filtered; in the filtrate the potassium is estimated, whilst the osmium is dried in a vacuum over phosphoric anhydride and weighed. The carbon was estimated by combustion, the volatile osmium tetroxide being retained by pumice steeped in hydrazine sulphate solution; no method is known of estimating hydrogen in an organic compound containing osmium.

Ammonium, rubidium, and *caesium osmylsalicylates* have compositions, aspects, and properties similar to those of the potassium salt.

Potassium nickelosalicylate, $\left[Ni<\left(\begin{matrix}O\cdot C_6H_4\\ O\cdot CO\end{matrix}\right)_2\right]K_2 + 4H_2O$, and *potassium cobaltosalicylate*, $Co(O\cdot C_6H_4\cdot CO_2K)_2,4H_2O$, were also obtained crystalline; they are only slightly soluble in water, which decomposes them. T. H. P.

Preparation of Calcium *o*-Acetoxybenzoate. J. A. WÜLFING (Eng. Pat., 1916, 100343; from *J. Soc. Chem. Ind.*, 1916, **35**, 944).—*o*-Acetoxybenzoic acid and calcium hydroxide are mixed intimately in equivalent proportions, and the mixture, moistened with a small amount of solvent, such as alcohol, ethyl acetate, or methyl ethyl ketone, is triturated until completely soluble in water. The solvent is then removed and the calcium salt is dried, disintegrated, and extracted with small quantities of ether until neutral. G. F. M.

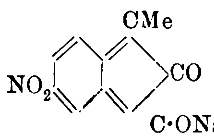
Preparation of Selenophthaleins and their Halogen Derivatives. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 291883; from *J. Soc. Chem. Ind.*, 1916, **35**, 922).—Selenium oxychloride may be used instead of selenium chloride for the production of phthaleins similar to those described in the chief patent (D.R.-P., 290540; this vol., i, 560). G. F. M.

Laurent's Benzimide (Benzylidenebenzaldehydecyanohydrin Acetal). MARIA SAVELSBERG (*J. pr. Chem.*, 1916, [ii], **93**, 271—276).—Laurent's "benzimide" has been obtained as a by-product in the preparation of mandelonitrile from the sodium hydrogen sulphite compound of benzaldehyde and aqueous potassium cyanide. Since it yields benzaldehyde, mandelic acid, and ammonia by hydrolysis with boiling dilute hydrochloric acid, it is regarded as an acetal with the constitution $CHPh(O\cdot CHPh\cdot CN)_2$. In accordance with this view, the substance has been obtained by condensing the calculated quantities of mandelonitrile and benzaldehyde in ethereal solution. C. S.

Influence of Sodium and Halogenated Alcohols [Alkyl Haloids] on Aldehydes, Ketones, etc. NAGAYOSHI NAGAI, AKIRA OGATA, and KAMETARO TAKATA (*J. Pharm. Chim.*, 1916, [vii], **14**, 215—216; from *Yakugakuzasshi*, 1916, **407**).—Schorigin (compare

A., 1907, i, 753; 1908, i, 866) obtained very poor yields in the action of sodium and alkyl haloids on acid chlorides, esters, and ketones. The authors have now improved the process in the case of ketones, obtaining a 60% yield of the tertiary alcohol, by carrying out the action in the presence of anhydrous ether. The ketones used were camphor, menthone, and benzyl methyl ketone. With aldehydes the reaction does not go so well, the yields varying from 6% to 31%. Using bromobenzene instead of ethyl iodide, slightly better yields were obtained. By passing a current of carbon dioxide through an ethereal solution of bromobenzene and sodium, a 7·5% yield of benzoic acid was obtained. W. G.

The Indene Series. II. Derivatives of 1:2-Diketo-3-methylhydrindene. J. VON BRAUN and K. HEIDER (*Ber.*, 1916, **49**, 1268—1282. Compare A., 1913, i, 1363).—In the earlier paper it was shown that a close analogy exists between isatin and 1:2-diketo-3-methylhydrindene, but the latter substance could only be obtained as a viscous oil which decomposed on heating. Search has now been made for crystalline derivatives of this which would serve to illustrate the above-mentioned analogy better. The 6-nitro- and 6-benzoylamino-derivatives are crystallisable, but the colours which they give in the indophenine reaction and on solution in alkalis are green, and not blue. The formation of the deeply coloured salts seems to be intimately connected with the fact that the mobile hydrogen atom is in tertiary combination, for 6-nitrohydrindone does not develop a deep colour in alkaline solution. As before, the difference is expressed by assuming the ortho-quinonoid configuration for the highly coloured enolate and the ordinary enol formulation for the hydrindone salts, thus:



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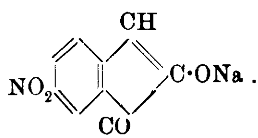

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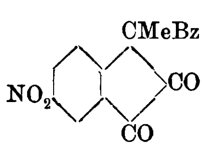
Chloroacetophenone is condensed with ethyl bromoacetate in the presence of zinc to form *ethyl β-hydroxy-β-*p*-chlorophenylpropionate*, $C_6H_4Cl·CH(OH)·CH_2·CO_2Et$, in 95% yield, as a colourless, stable oil, b. p. 176°/18 mm.; the corresponding *acid* separates in brilliant crystals, m. p. 109°. When the ester is boiled with formic acid, it changes into an oil, which yields p-*chloro-β-methylcinnamic acid*, $C_6H_4Cl·CMe{:}CH·CO_2H$, on hydrolysis with 10% sodium hydroxide. Two forms of this were observed, namely, glistening needles, m. p. 133·5°, and more soluble (in ether–light petroleum mixtures) nodules, m. p. 96—106°. The former is transformed into the latter on boiling with water; they both form the same *dibromide*, colourless needles, m. p. 126° (decomp.), and *ethyl ester*, b. p. 164—166°/12 mm., and they are both reduced slowly by hydrogen in the presence of palladium to *β-*p*-chlorophenylbutyric acid*, $C_6H_4Cl·CHMe·CH_2·CO_2H$, which forms a mass of crystals, m. p. 81°. This acid is more easily obtained by reducing the above

ester to *ethyl β-p-chlorophenylbutyrate*, b. p. 128—134°/12 mm., and hydrolysing this. The *chloride*, $C_6H_4Cl{\cdot}CHMe{\cdot}CH_2{\cdot}COCl$, b. p. 156—158°/18 mm., is condensed to *6-chloro-3-methylhydrindone*, $C_6H_3Cl{<}{\begin{smallmatrix}CHMe\\CO\text{——}\end{smallmatrix}}{>}CH_2$, b. p. 140°/8 mm., in the usual way. The latter compound forms a *semicarbazone*, m. p. 198—199°, and an *oximino*-derivative, $C_6H_3Cl{<}{\begin{smallmatrix}CHMe\\CO\text{——}\end{smallmatrix}}{>}C{:}N{\cdot}OH$, m. p. 171°, the *benzoate* of which has m. p. 144°. The oximino-compound is very quickly hydrolysed by hydrochloric acid and formaldehyde at 50°, to form *6-chloro-3-methylindan-1 : 2-dione*, $C_6H_3Cl{<}{\begin{smallmatrix}CHMe\\CO\text{——}\end{smallmatrix}}{>}CO$, which can only be isolated as an impure, vitreous, red mass. It dissolves in alkali hydroxides with a deep violet colour, gives a striking indophenine reaction, and forms a crystalline *disemicarbazone*, m. p. 269°.

For the preparation of the corresponding 6-nitro-compound, β-*p*-nitrophenylbutyric acid (Schröter, A., 1907, i, 531) was converted into the *chloride*, $NO_2{\cdot}C_6H_4{\cdot}CHMe{\cdot}CH_2{\cdot}COCl$, m. p. 58°, b. p. 190—200°/17 mm., and this was heated with aluminium chloride as usual, but the desired hydrindone could not be isolated from the product. *6-Nitro-3-methylhydrindone* is easily obtained, however, by dissolving 3-methylhydrindone in nitric acid (D 1·5) at 10—15°. It has m. p. 80°, and forms a *semicarbazone*, m. p. 253—254°, an *oxime*, m. p. 169°, a *2-benzylidene* compound, m. p. 131—132°, and a *2-oximino*-derivative, m. p. 165—166°, the *benzoate* of which has m. p. 140°. The oximino-compound also yields the *di-oxime*, $NO_2{\cdot}C_6H_3{<}{\begin{smallmatrix}CHMe\text{——}\\C({:}N{\cdot}OH)\end{smallmatrix}}{>}C{:}N{\cdot}OH$, m. p. 212°, and may be hydrolysed as above to form *6-nitro-3-methylindan-1 : 2-dione*, which crystallises as a dark red powder, m. p. 165—166°. This forms a reddish-brown *phenylhydrazone*, $C_{16}H_{13}O_3N_3$, m. p. 164°, and a pale green *quinoxaline* derivative, $C_{16}H_{11}O_2N_3$, m. p. 228—229°, and when the deep green solution in sodium hydroxide is shaken with benzoyl chloride there is formed the *benzoyl* derivative (I), yellow needles, m. p. 164°, and the *acid* (II), m. p. 95—96°:



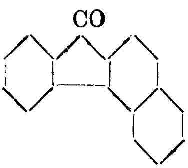
(I.)

(II.)

When hydrindone is nitrated, the chief product is 6-nitrohydrindone, but this is very difficult to purify (Kipping, T., 1894, **65**, 495). The crude product cannot be very impure, however, for it may be converted by means of amyl nitrite and alcoholic hydrochloric acid into the *2-oximino*-compound, pale yellow needles, m. p. 196°, without trouble, and this may be hydrolysed readily to *6-nitroindan-1 : 2-dione*, which is a dark brown substance.

6-*Amino*-3-*methylhydrindone*, $NH_2\cdot C_6H_3<\begin{matrix}CHMe\\CO\text{——}\end{matrix}>CH_2$, is easily obtained by reducing the corresponding nitro-compound, in the form of yellow needles, m. p. 103·5°. It yields a *hydrochloride;* a *picrate*, m. p. 144°; a *phenylthiocarbamide*, m. p. 181·5°; an *oxime*, m. p. 145·5°; an *acetyl* derivative, m. p. 182°; and a *benzoyl* derivative, m. p. 181°. The two acyl derivatives form oximino-compounds; 6-*acetylamino*-2-*oximino*-3-*methylhydrindone* decomposes at above 220°, and is not very stable, but the *benzoyl* compound, $NHBz\cdot C_6H_3<\begin{matrix}CHMe\\CO\text{——}\end{matrix}>C:N\cdot OH$, m. p. 229° (decomp.), may be hydrolysed to 6-*benzoylamino*-3-*methylindan*-1 : 2-*dione*, which is a reddish-brown powder, m. p. 133—135°, and yields a *diphenylhydrazone*, $C_{29}H_{25}ON_5$, m. p. 166—170°, and a *quinoxaline* compound, $C_{23}H_{17}ON_3$, m. p. 177—180°. J. C. W.

Preparation of 3 : 4-Benzofluorenone (*allo*Chrysoketone) and its Ability to Form a Metastable Variety. ALFRED SCHAARSCHMIDT (*Ber.*, 1916, **49**, 1444—1451).—Of the three possible benzofluorenones, the 1 : 2-member (chrysoketone) and the 2 : 3-isomeride (*iso*chrysoketone) are known, whilst the 1-carboxy-derivative of the 3 : 4-compound (*allo*chrysoketone) may easily be obtained (this vol., i, 47). If this acid is quickly heated over a free flame, it yields the remaining 3 : 4-*benzofluorenone* (allo*chrysoketone*) (annexed formula). Hot solutions of this deposit yellow needles on cooling quickly, but these change in contact with the cold solvent into orange rhombohedra, m. p. 161°. The stable form separates directly if the cooling and evaporation are slow. The *phenylhydrazone* is yellow and has m. p. 180°, whilst the *oxime* has m. p. 215°. J. C. W.

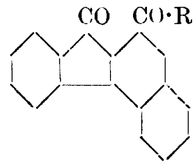


The Cause of the Abnormal Colour of Derivatives of *allo*Chrysoketone (3 : 4-Benzofluorenone). ALFRED SCHAARSCHMIDT and N. IRINEU (*Ber.*, 1916, **49**, 1451—1460).—Some new derivatives of *allo*chrysoketone-1-carboxylic acid have been prepared. It is found that whereas the acid is red, some derivatives (ester and amide) are orange, whilst others (methylamide, etc.) are yellow. Taken in conjunction with the discovery that the parent ketone itself exists in orange and red forms (preceding abstract), it is suggested that the orange-coloured derivatives are quinonoid, whilst the yellow are benzenoid in structure, the enhancement of the colour to red in the case of the free acid being accounted for by assuming inner-salt formation between the carboxyl and the carbonyl groups.

allo*Chrysoketone*-1-*carboxylamide* (1-*amino*-3 : 4-*benzofluorenone*), prepared from the chloride, forms reddish-orange needles, m. p. 285°, after becoming yellow at 220°. The *methylamide* usually crystallises in long, pale yellow needles, m. p. 222°, but glacial acetic acid solutions deposit stout, scarlet needles which, however,

cannot be preserved out of contact with the solvent. The *dimethylamide* forms yellow crystals, m. p. 219—220°. The *anilide*, m. p. 226—227°, and the *diphenylamide*, m. p. 295—296°, are orange-yellow. 1-Aminoanthraquinone also reacts with the chloride to form 1 : 1′-*anthraquinonylamino*-3 : 4-*benzofluorenone*, which is a yellow powder, and dyes cotton yellow from its violet-red hyposulphite vat.

The above amides are represented by the annexed formula, where R = NH_2,NHMe,NMe_2,NHPh,NPh_2 or $NH\cdot C_6H_3<\substack{CO \\ CO}>C_6H_4$.



J. C. W.

Preparation of Anthraquinone. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 292681; from *J. Soc. Chem. Ind.*, 1916, **35**, 921).—Anthracene may be oxidised to anthraquinone by oxygen under pressure in presence of a catalyst by the following procedure: 100 parts of 30% aqueous anthraquinone paste is mixed with 3000 parts of water, 250 parts of 25% ammonia, and 5 parts of copper oxide in an autoclave, and a quantity of oxygen corresponding with 3 atoms per molecule of anthracene is forced in, the mass being stirred and heated for twenty hours at 170°. The anthraquinone separates on cooling, and is washed free from copper compounds with ammoniacal water. Nickel, cobalt, iron, or lead compounds may be used as catalysts instead of copper oxide. G. F. M.

The Volatile Oil from the Wood of the Indian Deodar Tree. OSWALD DIGBY ROBERTS (T., 1916, **109**, 791—796).—The volatile oil of the wood *Cedrus Deodara*, Loud. (compare Schimmel & Co., A., 1915, i, 826), was separated into several fractions by distillation under atmospheric pressure. The first fraction, b. p. 230—260°, contained a ketone, the odour of which characterised the original oil, and also a small quantity of a phenol (benzoyl derivative, needles, m. p. 70°), which produced a deep, blood-red coloration with ferric chloride in alcoholic solution. The ketone, $C_9H_{14}O$, was probably *p*-methyl-Δ^3-tetrahydroacetophenone; it gave a dibromo-oxime, m. p. near 130°, and a semicarbazone, leaflets, m. p. 163—164°, the latter on hydrolysis with dilute sulphuric acid yielding a ketone, apparently *p*-tolyl methyl ketone, b. p. 222—224°, n_D^{20} 1·4965; semicarbazone, m. p. 204—205°. There were also present in the oil esters of hexoic, heptoic, and stearic acids, together with sesquiterpenes consisting mainly of a *d*-sesquiterpene, b. p. 151—153°/19 mm., 262—265° under atmospheric pressure, D_{15}^{15} 0·9276, n_D^{21} 1·5170, α_D variable. Sesquiterpene alcohols and high-boiling, viscous decomposition products appeared to constitute the remainder of the oil. D. F. T.

Amber (Succinite). A. Tschirch and Cornelis de Jong (*Arch. Pharm.*, 1915, **253**, 290—305. Compare A., 1895, i, 384).—Two samples of crude succinoabietic acid, prepared twenty-one years ago (*loc. cit.*), dissolved in ether to the extent of about 15% and about 10% respectively. The ethereal solutions, examined by Tschirch's extraction method, gave the following results: (1) 1% ammonium carbonate extracted an *acid*, $C_{20}H_{30}O_4$, m. p. 120°, acid number 147·21 (direct) and 151·80 (indirect), saponification number 155·15 (cold) and 174·18 (hot), and iodine number 18·60, which is named *succoxyabietic acid*; (2) 1% sodium carbonate extracted an *acid*, $C_{40}H_{60}O_5$, m. p. 110° and 112° (from the two samples), acid number 88·63 and 91·21 (direct) or 92·61 and 94·81 (indirect), saponification number 97·03 and 97·43 (cold) or 141·93 and 144·34 (hot), and iodine number 47·71 and 50·56, which is named *succinoabietolic acid*; (3) 1% potassium hydroxide extracted succinoabietolic acid (present as the bornyl ester, since the odour of borneol was observed). Succinoabietolic acid is hydrolysed by alcoholic $N/2$-potassium hydroxide, and yields succinosilvic acid, succinoabietol, borneol, and carbonic acid: $2C_{40}H_{60}O_5 + 2H_2O = 2C_{24}H_{36}O_2 + C_{20}H_{30}O + C_{10}H_{18}O + 2H_2CO_3$.

Amber itself has been examined by the extraction method. The portion soluble in alcohol (about 30% of the whole) contains succoxyabietic acid and succinoabietolic acid (the so-called succinoabietic acid is a mixture of these two acids). Succinin, the portion (about 70%) of amber which is insoluble in alcohol, consists of a saponifiable constituent (which yields succinic acid and succinoresinol by hydrolysis with alcoholic $N/2$-potassium hydroxide) and mainly of an unsaponifiable constituent, *succinoresin*, a yellow powder. C. S.

The Vulcanisation of Caoutchouc and the Possibility of its Regeneration from "Vulcanisates." II. C. Harries and Ewald Fonrobert (*Ber.*, 1916, **49**, 1390—1398. Compare this vol., i, 659).—Experimental evidence is given in support of the statements with regard to some of the differences between natural Para caoutchouc, a fresh vulcanisate prepared by the hot method and then almost deprived of sulphur by extraction with acetone, and an old vulcanisate, one, that is, that has suffered "after vulcanisation."

The question is raised whether the action of sulphur causes a migration of an ethylene linking, and answered in the negative by studying the products of the hydrolysis of the ozonides. The desulphurised vulcanisate is much less quickly acted on by ozone, and so changes largely to an oxozonide which chiefly yields acids on hydrolysis. The same acids or their aldehydes are obtained from natural caoutchouc, representatives of lower states of oxidation predominating. Lævulaldehyde, formic, acetic, lævulic, and succinic acids, and ethyl lævulate were characterised in the case of the regenerate, but not methyl*cyclo*hexanone, which would have indicated the suggested isomerism. J. C. W.

Saponin from the Epicarp of Sapindus Mukurosi Gaert. YASUHIKO ASAHINA and TORAJI SHIMIDZU (*J. Pharm. Chim.*, 1916, [vii], **14**, 188—190; from *Yakugakuzasshi*, 1916).—This saponin was separated as an amorphous, white powder, $[\alpha]_D^{20}$ +13·28. It is soluble in alcohol, very slightly soluble in water, and insoluble in chloroform, ether, acetone, and light petroleum. When hydrolysed, it yields *d*-arabinose and a sapogenin. The latter crystallises from alcohol in the form of small plates, m. p. 319°. The sapogenin yields crystalline potassium and barium compounds, a triacetyl compound, m. p. 167°, a benzoyl compound, m. p. 107°, and a methyl ester, m. p. 218°. Both the saponin and sapogenin, when dissolved in acetic anhydride and the solution treated with a drop of sulphuric acid, yield a bright reddish-violet coloration.

W. P. S.

A Chemical Paradox. I. M. KOLTHOFF (*Chem. Weekblad*, 1916, **13**, 1016—1019).—The author attributes the chemical paradox described by de Vries (this vol., i, 56) to the presence of a basic zinc salt, Zn(OH)Cl. A. J. W.

Synthesis of 2 : 3-Dihydroxyphenylacetic Acid. W. MOSIMANN and J. TAMBOR (*Ber.*, 1916, **49**, 1258—1261).—Attempts have been made to hydrolyse 2:3-dimethoxymandelonitrile (von Krannichfeldt, A., 1914, i, 190) to 2:3-dihydroxyphenylacetic acid by heating it with hydrobromic or hydriodic acids, but the chief products of the action are found to be 2-*hydroxy*-3-*methoxyphenylacetic acid*, rhombic tablets, m. p. 124°, and 7-*hydroxy*iso*coumaranone*, $OH\cdot C_6H_3<\begin{matrix}O\\CH_2\end{matrix}>CO$, white needles on sublimation, m. p. 189°, or pointed leaflets from hot water. The latter may be converted into 7-*methoxy*iso*coumaranone*, rhombic leaflets, m. p. 80°, by means of diazomethane; into 7-*acetoxy*iso*coumaranone*, prisms, m. p. 133°, by the addition of a drop of concentrated sulphuric acid to a solution in acetic anhydride; and into 7-*acetoxy*-3:3-*diacetyl*iso*coumaranone*, $OAc\cdot C_6H_3<\begin{matrix}O\\CAc_2\end{matrix}>CO$, microscopic leaflets, by boiling with acetic anhydride and sodium acetate. It also yields a small amount of 2:3-*dihydroxyphenylacetic acid*,

$$C_6H_3(OH)_2\cdot CH_2\cdot CO_2H,\tfrac{1}{2}H_2O,$$

white needles, m. p. 75°, anhydrous substance, m. p. 103—104°, on boiling with concentrated sodium carbonate. J. C. W.

***o*-Vanillin.** W. MOSIMANN and J. TAMBOR (*Ber.*, 1916, **49**, 1261—1265).—Some new derivatives of *o*-vanillin have been isolated during attempted syntheses of 2:3-dihydroxyacetophenone (A., 1914, i, 190) and 2:3-dihydroxyphenylacetic acid.

Methyl carbonato-o-vanillin [$OMe:O\cdot CO_2Me:CHO=1:2:3$] is obtained in microscopic tablets, m. p. 59° (decomp.) by the action of methyl chloroformate on *o*-vanillin in the presence of *N*-sodium hydroxide.

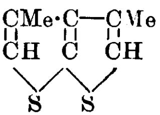
o-Homoveratrole [$Me:OMe:OMe=1:2:3$] is prepared by reduc-

ing *o*-veratraldehyde with amalgamated zinc and boiling hydrochloric acid; it is a refractive, aromatic oil, b. p. 92—93°/18 mm. 2:3-Dimethoxy- and 2:3-dihydroxyacetophenone are also reduced by Clemmensen's method to 2 : 3-*dimethoxy*-1-*ethylbenzene*, a mobile, faintly aromatic oil, b. p. 95—96°/19 mm., and 2:3-*dihydroxy*-1-*ethylbenzene*, a refractive oil, b. p. 130—131°/15 mm.

On bromination, 2:3-dimethoxyacetophenone yields ω-*bromo*-2:3-*dimethoxyacetophenone*, in prisms, m. p. 53—54°, and the ωω-*dibromo*-compound, $C_6H_3(OMe)_2\cdot CO\cdot CHBr_2$, hexagonal tablets, m. p. 67—68°, according to the proportion of bromine used. Both compounds yield o-*veratric acid* [OMe:OMe:CO_2H=1:2:3] white needles, m. p. 122°, on oxidation. Similarly, ω-*bromo*-2:3-*diacetoxyacetophenone* is obtained by bromination, in white needles, m. p. 97—98°, and this is converted by boiling with a suspension of chalk in water into 7-*hydroxycoumaranone*, $OH\cdot C_6H_3<{}^{CO}_{O}>CH_2$, stout, brown crystals, m. p. 184° (decomp.).

7-Methoxy*iso*coumaranone (preceding abstract) condenses with aldehydes; with *o*-veratraldehyde it forms 7:2′:3′-*trimethoxy*-3-*benzylidene*iso*coumaranone*, $OMe\cdot C_6H_3<{}^{O\cdot CO}_{C:CH\cdot C_6H_3(OMe)_2}$, yellow needles, m. p. 183—184°; with aceto-*o*-vanillin it yields 2′-*acetoxy*-7 : 3′-*dimethoxy*-3-*benzylidene*iso*coumaranone*, pale yellow leaflets, m. p. 136—137°; with piperonaldehyde it gives 7-*methoxy*-3′ : 4′-*methylenedioxy*-3-*benzylidene*iso*coumaranone*, microscopic, yellow prisms, m. p. 185°. J. C. W.

Action of Sulphur on *n*-Octane under Pressure. WALTER FRIEDMANN (*Ber.*, 1916, **49**, 1344—1352).—When *n*-octane is heated with sulphur for some hours at 270—280° in a sealed tube, it is converted into a thiophen, $C_8H_{12}S$, and a thiophthen, $C_8H_8S_2$, and about 15% is carbonised. The yields of these cyclic compounds are small, and their formation is supposed to be due to a preliminary rearrangement of *n*-octane into a branched-chain octane, thus: $C_8H_{18} \longrightarrow CHMe_2\cdot CHMe\cdot CHMe_2$; and this $+ 6S$ would readily give $4H_2S$ + the compound with the annexed formula.


$+ 4H_2S$

The *thiophen* derivative, $C_8H_{12}S$, has b. p. 179—180°, D^{21} 0·9386, forms crystalline compounds with mercuric chloride, and reacts with bromine water to form the *dibromide*, $C_8H_{10}Br_2S$, b. p. 250—254°, with acetyl chloride to yield the *compound*, $C_{10}H_{14}OS$, b. p. 252—254°, D^{20} 1·205, and with propionyl chloride to give the *compound*, $C_{11}H_{16}OS$, a fruity, yellow oil, b. p. 260—263°. In many respects it resembles Muhlert's diethylthiophen (1886).

The *thiophthen* derivative, $C_8H_8S_2$, separates in long, monoclinic crystals, like isinglass, m. p. 116—117°, and forms a *picrate*, deep red needles, m. p. 127—128°, and a *dibromide*, $C_8H_6Br_2S_2$, slender needles, m. p. 170°.

If octane itself is heated at 280° in a sealed tube, oils of lower boiling point (118° upwards) are formed. J. C. W.

Action of Sulphur on 2-Methylnaphthalene under Pressure. WALTER FRIEDMANN (*Ber.*, 1916, **49**, 1352—1355. Compare this vol., i, 382).—The proportion of sulphur derivatives to simple hydrocarbons, which are formed when the methylnaphthalenes are heated with sulphur at about 300° under pressure, varies according to whether the pressure in the tubes is occasionally released or not. If 1-methylnaphthalene is heated continuously for three days, a *compound*, $C_{22}H_{14}S_2$, is formed, which crystallises from cumene in long needles, m. p. 332°. 2-Methylnaphthalene yields an isomeric *compound*, pale yellow needles, m. p. 350°, for which also cumene is the only available solvent, mixed with a *compound*, $C_{22}H_{14}S$, yellow leaflets, m. p. 167°, soluble in benzene, but not in alcohol, also with *αβ-di-β-naphthylethane*, colourless, slender needles, m. p. 182° (orange-yellow *dipicrate*, m. p. 198°), and with β-dinaphthastilbene, m. p. 254° (*tripicrate*, red needles, m. p. 215°).

The compound, m. p. 253°, described by Bamberger and Lotter (1888) as αβ-di-β-naphthylethane, was most probably β-dinaphthastilbene. J. C. W.

Mercuric Acetate as an Oxidising Agent in Alkaloidal Chemistry. J. GADAMER (*Arch. Pharm.*, 1915, **253**, 274—289).—The experiences of Tafel (1892), Reissert (1894), and Balbiano and Paolini (1903) show that mercuric acetate is a mild oxidising agent, an excess of which and its products of reduction are easily removed from the system. The author finds that in alkaloidal chemistry the reagent has not only a qualitative, but also a quantitative, value, since the resulting sparingly soluble mercurous acetate can be collected and weighed.

[With FRITZ KUNTZE.]—According to the amount of iodine used, the authors had found (A., 1911, i, 1012) that the oxidation of *N*-methylbulbocapnine by alcoholic iodine apparently proceeds in the sense of the equation: $C_{20}H_{21}O_4N+4I=C_{20}H_{18}O_4NI+3HI$. They now find that a di- instead of a tetra-dehydro-derivative is produced when the oxidation is effected in dilute acetic acid by mercuric acetate at the ordinary temperature: $C_{20}H_{21}O_4N+2Hg(OAc)_2=C_{20}H_{19}O_4N+2HOAc+Hg_2(OAc)_2$. A deeper-seated oxidation also proceeds to some extent, and this becomes more marked when the oxidation is effected on the water-bath, the amount of mercurous acetate obtained indicating a consumption of 3 mols. of mercuric acetate.

By oxidation in a similar manner at the ordinary temperature *d*-canadine is converted into berberine, and corydaline also loses four atoms of hydrogen. In the latter case the oxidation proceeds in two stages, a di- and a tetra-dehydrocorydaline being obtained. Since the optical activity of the alkaloid disappears with the first pair of hydrogen atoms, the two asymmetric carbon atoms in corydaline would appear to be contiguous, and the author is constrained to bring again under consideration a formula of the alkaloid which he rejected in 1902 on the ground of improbability.

[With R. Kondo.]—The oxidation of *r*-laudanosine by mercuric acetate yields the same products as Pyman obtained with manganese dioxide and dilute sulphuric acid (T., 1909, **95**, 1266), namely, veratraldehyde and 4 : 5-dimethoxy-2-β-methylaminoethylbenzaldehyde. The non-nitrogenous substance, $C_{14}H_8(OMe)_4$, mentioned by Pyman is produced in considerable quantity, and appears to be tetramethoxydibenzyl, $C_{14}H_{10}(OMe)_4$.

[With Schulemann.]—The oxidation of papaverine by mercuric acetate yields papaveraldine, dimethoxycinchonic acid, and about 10% of papaverinol, which thus becomes a comparatively easily obtainable substance. When papaverine and mercuric acetate are mixed in equivalent quantities a clear solution is obtained, from which a white precipitate containing non-ionisable mercury is thrown down by sodium chloride. The clear solution therefore probably contains a mercuriacetate, this group having entered at the methylene bridge. The substance is not very stable, however, and reacts with a further quantity of mercuric acetate to form mercurous acetate, acetic acid, and papaverinol. C. S.

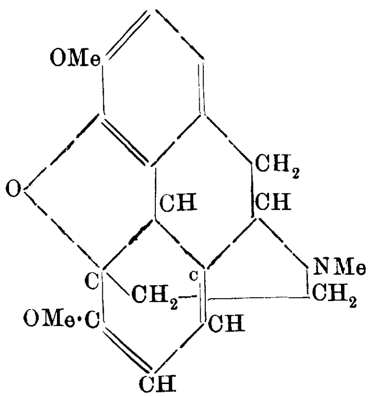
Hofmann's Degradation of Alkaloids of the Phenanthrene (*apo*Morphine) Series. J. Gadamer [and in part, Fritz Kuntze and R. Kondo] (*Arch. Pharm.*, 1915, **253**, 266—273).—Since *iso*thebaine and *iso*bebeerine each yield a pair of des-bases by degradation, the heterocyclic ring undergoing rupture on each side of the nitrogen atom, it is remarkable that the quaternary ammonium derivatives of *apo*morphine, bulbocapnine (Gadamer and Kuntze, A., 1911, i, 1012), and corytuberine (*ibid.*, i, 1011) should, according to observations hitherto recorded, undergo rupture in only one of the two possible ways. The author, in conjunction with Kuntze and Kondo, now finds that a pair of methine bases is formed in each of these three cases also, one of which is, of course, optically inactive and the other optically active.

N-Methylbulbocapnine methosulphate is boiled with aqueous sodium hydroxide, and the resulting mixture of methine bases is isolated in ethereal solution. By treatment of this solution with methyl sulphate or with methyl iodide and crystallisation of the resulting salts, the methosulphates from water and the methiodides from 50(vol.)% alcohol, the optically inactive methine base can be isolated. The active base, which is strongly lævorotatory, is obtained in colourless, stout plates by crystallising the mixture of methine bases from methyl alcohol.

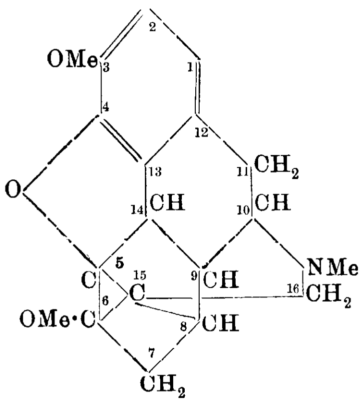
In a similar manner, *N*-methyl*apo*morphine methosulphate is degraded into a mixture of two methine bases, which are separated by a systematic fractional extraction of the ethereal solution with *N*-hydrochloric acid. The inactive base, which is the stronger, forms a *hydrochloride*, slender needles, which is sparingly soluble in cold alcohol and is optically inactive in a 2% solution. The m. p. and the rotatory power (the highest value of $[\alpha]_D$ obtained is $+138{\cdot}6°$ in ethereal solution) of the pure active base have not yet been determined; its hydrochloride is easily soluble in alcohol.

C. S.

Thebaine. V. Reduction of Thebaine and Phenyldihydrothebaine. MARTIN FREUND and EDMUND SPEYER (*Ber.*, 1916, **49**, 1287—1307. Compare A., 1906, i, 303, etc.).—Recent researches of von Braun and Gadamer have disclosed facts which cannot be reconciled with Knorr's formulæ for the morphine alkaloids, and other contradictory evidence is now put forward. In Knorr's formula for thebaine (I) there are two aliphatic double linkings, and the chief question raised in the present paper is whether these really exist. As thebaine is very unstable in acid solutions, most of the methods for saturating double linkings cannot be applied, and, unfortunately, reduction with sodium and alcohol does no more than to rupture the oxide ring. Phenyldihydrothebaine, however, is more stable, and as it must be very closely related to thebaine, being obtained merely by the action of magnesium phenyl bromide, conclusions drawn from experiments with it may be justly carried over to the parent base. It is not even attacked during electrolytic reduction, but hydrogenation in the presence of palladium leads to the formation of a secondary base, that is, to the opening of the nitrogen ring. There is certainly no evidence of the presence of ethylenic linkings, and the alternative formula (II) is therefore proposed for thebaine. Similar formulæ are suggested for morphine and codeine, and many reactions are discussed which can be explained by them.



(I.)



(II.)

The product of the reduction of phenyldihydrothebaine is termed *phenyltetrahydrothebaimine*, ($C_{25}H_{27}O_3N \longrightarrow C_{24}H_{25}O_3\cdot NHMe$). It crystallises in leaflets, m. p. 122°, α_D +27·6° (in dilute acetic acid), and forms a *nitroso*-compound, red crystals, decomp. 193°. It reacts with carbonyl chloride to form the *carbamide*, $CO[C_{24}H_{25}O_3\cdot NMe]_2$, in felted needles, m. p. 138—139°, and with methyl iodide to form *phenyltetrahydrothebaiminmethine methiodide*, $C_{27}H_{34}O_3NI$, in jagged columns, m. p. 233—235°. This loses trimethylamine on boiling with dilute sodium ethoxide, leaving *phenyltetrahydrothebenol*, $C_{22}H_{18}O(OMe)_2$, which crystallises in columns, m. p. 86°. The secondary base also reacts with methyl *p*-toluenesulphonate to

form the *compound*, $C_{24}H_{25}O_3\cdot NMe_3\cdot SO_3\cdot C_7H_7$, needles, m. p. 245°, which is hydrolysed by boiling alcoholic sodium hydroxide to trimethylamine and the above thebenol.

Phenyldihydrothebaine is chlorinated by adding 30% hydrogen peroxide to a boiling solution in hydrochloric acid. *Dichlorophenyldihydrothebaine*, $C_{25}H_{27}O_3NCl_2$, forms nodules of crystals, m. p. 135—140°, and gives a *hydriodide*, B,HI,H_2O, hexagonal leaflets, m. p. 203°, and a *methiodide*, nodules of small rods, m. p. 230°. The latter yields des-N-*methyldichlorophenyldihydrothebaine hydriodide*, $C_{25}H_{26}O_3NCl_2Me,HI$, on warming with sodium ethoxide, in felted needles, m. p. 205°, and this forms a methiodide which is hydrolysed by sodium ethoxide to *dichlorophenyldihydrothebenol*, $C_{24}H_{22}O_3Cl_2$, needles, m. p. 160—162°.

Dibromophenyldihydrothebaine is obtained by the action of a solution of bromine in acetic acid, mixed with concentrated hydrobromic acid. It crystallises in needles, m. p. 165—168°, and yields a *perbromide*, decomp. 195—196°, a *hydrobromide*, m. p. 198°, and a *hydriodide*, m. p. 205—208°. The hydrobromide suffers debromination at a lead cathode in 20% sulphuric acid to form *phenyltetrahydrothebaine*, $C_{25}H_{29}O_3N$, a pale yellow oil, which yields a *hydrobromide*, leaflets, decomp. 175—176°, and a *methiodide*, m. p. 215°, and is converted by boiling with hydriodic acid into *norphenyltetrahydrothebaine hydriodide*, $C_{23}H_{25}O_3N,HI$, felted needles, decomp. 195°.

Acetylphenyldihydrothebaine yields an indefinite, non-basic product, m. p. about 90°, on warming with cyanogen bromide dissolved in chloroform.

Phenyldihydrothebaine is oxidised to *phenyldihydrothebaic acid*, $C_{24}H_{25}O_5N$, by an alkaline solution of hydrogen peroxide. This crystallises in jagged columns, decomp. 243—245°, and forms a *barium* salt, $C_{24}H_{23}O_5NBa$, decomp. 280°. J. C. W.

Some Derivatives of Pyridine and Quinoline. ED. STEINHÄUSER and E. DIEPOLDER (*J. pr. Chem.*, 1916, [ii], **93**, 387—400).—It has already been shown that the action of phosphorus pentachloride on 1-methyl-2-pyridone in the presence of phosphoryl chloride yields a small quantity of a dichloro-compound in addition to the expected 2-chloropyridine (Fischer, A., 1899, i, 633); it is now shown that the formation of the former substance is favoured by a higher temperature and by a considerable reduction in the quantity of the phosphoryl chloride (compare Sell and Dootson, T., 1898, **73**, 432). The dichloropyridine is a colourless, crystalline solid of sweet odour, m. p. 59—60°, insoluble in dilute hydrochloric acid; *mercurichloride*, colourless needles, m. p. 192—193°.

2-Aminopyridine undergoes condensation with aldehydes, giving compounds which contain equimolecular proportions of base and aldehyde in the case of aromatic aldehydes, excepting benzaldehyde, which resembles the fatty aldehydes in combining with the aminopyridine in the molecular proportion 2:1. *Trichloroethylidenediaminodipyridine*, $C_{12}H_{11}N_4Cl_3$, obtained from aminopyridine and chloral, forms colourless needles, m. p. 160°. *Benzylidenediamino-*

dipyridine, $C_{17}H_{16}N_4$, obtained from the aminopyridine and benzaldehyde, forms needles, m. p. 105—106°. *o*-Hydroxybenzylideneaminopyridine, derived from *o*-hydroxybenzaldehyde, was found to have m. p. 66—67°, instead of 69°, as stated earlier (Fischer, *loc. cit.*).

When heated with barium oxide and chloropyridine at 200—220° for eight hours, 2-aminopyridine was converted into 2 : 2'-*dipyridylamine*, $C_{10}H_9N_3$, colourless needles or prisms, m. p. 94—95°; *hydrochloride*, needles, m. p. 115°; *mercurichloride*, colourless needles, m. p. 206°; *aurichloride*, yellow needles, m. p. 245°; *platinichloride*, ochre-yellow, microscopic needles, m. p. 160° (decomp.), after sintering at 135°; *picrate*, yellow needles, m. p. 225°, after sintering at 215°. In the absence of barium oxide, the product of the interaction of *o*-aminophenol and 2-chloropyridine was 2-o-*hydroxyphenylimino*-1 : 2-*dihydropyridine*, $OH\cdot C_6H_4\cdot N\colon C<\begin{matrix}CH{=}CH\\NH\cdot CH\end{matrix}>CH$, yellow prisms, m. p. 87—89°, which was accompanied by a small quantity of a colourless substance, m. p. 154°, probably the isomeric 2-*o*-hydroxyphenylaminopyridine.

The reaction product of 2-chloropyridine and *o*-anisidine at 210° in the presence of barium oxide was 2-o-*methoxyphenylaminopyridine*, $OMe\cdot C_6H_4\cdot NH\cdot C_5H_4N$, colourless leaflets or rhombohedra, m. p. 92°; *hydrochloride*, colourless prisms, m. p. 175°, after sintering at 170°; *nitrosoamine*, needles, m. p. 121°. When heated with concentrated hydrochloric acid at 195°, the methoxyphenylaminopyridine undergoes scission of the methyl group with formation of the above-described hydroxyphenyliminodihydropyridine. In the absence of barium oxide, the action of the chloropyridine and anisidine yielded 2-o-*hydroxyphenylimino*-1-*methyl*-1 : 2-*dihydropyridine*, $OH\cdot C_6H_4\cdot N\colon C<\begin{matrix}CH{=}CH\\NMe\cdot CH\end{matrix}>CH$, pale yellow needles, m. p. 159°; *hydrochloride*, colourless needles, m. p. 255°, after sintering at 245°. These results supply confirmatory evidence of the constitution suggested above for the substance produced by the interaction of aminophenol and chloropyridine in the absence of barium oxide, and still further evidence is forthcoming in the conversion of 2-phenylaminopyridinium methiodide by sodium hydroxide solution into 2-*phenylimino*-1-*methyl*-1 : 2-*dihydropyridine*,

$$NPh\colon C<\begin{matrix}CH{=}CH\\NMe\cdot CH\end{matrix}>CH,$$

yellow crystals, m. p. 60—67°.

In order to eliminate the possibility that the methyl radicle which migrated in the above reaction had become attached to the internuclear nitrogen atom, a mixture of methyl-*o*-anisidine, 2-chloropyridine, and barium oxide was heated at 250°, when 2-o-*methoxyphenylmethylaminopyridine*, $OMe\cdot C_6H_4\cdot NMe\cdot C_5H_4N$, colourless, rhombohedral crystals, m. p. 30°, b. p. 155—175° in a vacuum, was obtained; *picrate*, compact, yellow needles, m. p. 143° after sintering at 130°. The colourless nature of this product provides a fairly convincing indication that the yellow reaction product of chloropyridine and anisidine is not of analogous struc-

ture. When heated with concentrated hydrochloric acid at 170°, the methoxyphenylmethylaminopyridine was converted into 2-o-*hydroxyphenylmethylaminopyridine*, $OH\cdot C_6H_4\cdot NMe\cdot C_5H_4N$, colourless prisms, m. p. 153°, which was also obtained by heating a mixture of 2-chloropyridine, *o*-methylaminophenol, and barium oxide at 205°.

2-o-*Methoxyphenylaminoquinoline*, $OMe\cdot C_6H_4\cdot NH\cdot C{<}\begin{matrix}CH{:}CH\\ N{-}C_6H_4\end{matrix}$, was obtained by allowing 2-chloroquinoline and *o*-anisidine to react in the presence of barium oxide at 190—200°; this forms colourless prisms and cubes, which melt at 100°, then resolidify, and re-melt at 113°; *nitrosoamine*, needles, m. p. indistinct at 120°; *picrate*, yellow needles, m. p. 220°. In the absence of barium oxide, the same reagents yielded 2-o-*hydroxyphenylimino*-1-*methyl*-1:2-*dihydroquinoline*, $OH\cdot C_6H_4\cdot N{:}C{<}\begin{matrix}CH{=}CH\\ NMe\cdot C_6H_4\end{matrix}$, yellow rhombohedra and prisms, m. p. indistinct between 90° and 135°.

D. F. T.

Electrolytic Preparation of 1-Methyl-2-pyridone and of some 1-Methylquinolones. Some Derivatives of 1-Methyl-2-pyridone. OTTO FISCHER and M. CHUR (*J. pr. Chem.*, 1916, [ii], **93**, 363—377).—The electrolytic method described by Fischer and Neundlinger (A., 1913, i, 1226) for the preparation of 1-methyl-2-pyridone from methylpyridinium salts has been found to yield uncertain and variable results, so that a further investigation of the necessary conditions was advisable.

Pure pyridine is converted into methylpyridinium sulphate by treatment with methyl sulphate (Decker and Kaufmann, A., 1911, i, 807). The product from 50 grams of pyridine and 80 grams of methyl sulphate is dissolved in 500 c.c. of water, treated with dilute sodium hydroxide solution, and then submitted to electrolytic oxidation in a cylindrical, porous cell. The anode is of fine iron gauze capable of being rotated, whilst the cathode is of iron sheet, the catholyte being a solution of sodium hydroxide. For the satisfactory progress of the oxidation process it is found necessary to have a little potassium ferricyanide present as catalyst in the anolyte, very little oxidation occurring in the absence of this substance. Details are given of the dimensions of the electrolytic apparatus. Yields of 1-methyl-2-pyridone amounting to 90—95% of the theoretical are obtainable.

The following derivatives of 1-methyl-2-pyridone are described: *picrate*, yellow needles, m. p. 145°; *hydrochloride*, colourless needles, m. p. 166°; *platinichloride*, orange-coloured needles, m. p. 141°; *hydrobromide*, prisms, m. p. 174°; *picrolonate*, brownish-yellow needles, m. p. 120°; *styphnate*, yellow needles, m. p. 162°. The methylpyridone forms *additive* compounds with a semimolecular proportion of quinol or *p*-nitrophenol, the products forming respectively prisms, m. p. 118°, and flat, hexagonal crystals, m. p. 62°. By treating 1-methyl-2-pyridone in sulphuric acid with a dilute solution of nitric acid in the same solvent, 3(?)-*nitro*-1-

methyl-2-pyridone is obtained as a yellow solid, m. p. 172°. When the nitration is effected in the absence of sulphuric acid by nitric acid of 62% concentration, the chief product is 3(?):5(?)-*dinitro-1-methyl-2-pyridone*, almost colourless needles or leaflets, m. p. 178°, which behaves as an acidic substance dissolving even in weak alkalis with formation of brownish-red solutions; *lead* salt, sparingly soluble, red substance; *mercury* salt, and *barium* salt, brownish-red precipitates; the dinitro-compound reduces alcoholic ammoniacal silver nitrate solution with production of a silver mirror. When a solution of the methylpyridone is submitted to the action of a current of chlorine, 3:5-*dichloro-1-methyl-2-pyridone*, colourless needles, m. p. 141°, is formed, the constitution of which is demonstrated by its yielding the known 2:3:5-trichloropyridine when treated with phosphorus pentachloride at 180°. The action of bromine on the methylpyridone produces 3:5-dibromo-1-methyl-2-pyridone, m. p. 180° (Decker and Kaufmann, *loc. cit.*, give 176°), which when heated with a mixture of phosphorus pentabromide and tribromide at 150° undergoes further conversion into 2:3:5-*tribromopyridine*, colourless needles, m. p. 46°, of an odour recalling bromoform; this substance is feebly basic, and its solution in concentrated hydrochloric acid decomposes when diluted with water; *mercurichloride*, $(C_5H_2NBr_3)_2HgCl_2$, a crystalline powder, m. p. 181—182°.

When heated with concentrated ammonia solution for several hours at 180—200°, the tribromopyridine is converted into 3:5-*dibromo-2-aminopyridine*, a mono-acid base, colourless needles, m. p. 105°; *hydrochloride*, needles, m. p. 193°; *aurichloride*, reddish-yellow, crystalline powder, m. p. 212°; *platinichloride*, yellow needles, decomp. at 285—315°; *mercurichloride*, colourless needles, m. p. 174°; *picrate*, yellow needles, m. p. 228°; *acetyl* derivative, needles, m. p. 102°; *benzoyl* derivative, needles, m. p. 142—143°; *salicylidene* derivative, orange-yellow needles, m. p. 162°.

In extension of the investigations of the oxidation of quinoline derivatives (Fischer and Neundlinger, *loc. cit.*; Neundlinger and Chur, A., 1914, i, 727), 8-methoxy- and 6-methoxy-1-methylquinoline were submitted to electrolytic oxidation in the manner above described for 1-methylpyridine. 8-Methoxy-1-methylquinoline, obtained as a crystalline solid, needles, m. p. 49—50° (compare Kaufmann and Rothlen, this vol., i, 417), on anodic treatment under a layer of ether, yielded 8-*methoxy-1-methyl-2-quinolone*, colourless prisms, m. p. 70°, whilst 6-methoxy-1-methylquinoline was converted into 6-*methoxy-1-methylquinolone*, colourless needles, m. p. 75—76°.

D. F. T.

Scission of the Dihydroindole Ring by Reduction. J. von Braun and L. Neumann (*Ber.*, 1916, **49**, 1283—1287).—Emde (A., 1912, i, 801) supposed that 1:1-dimethyltetrahydroquinolinium chloride yields dimethyl-*o*-propylaniline on treatment with sodium amalgam, but it was recently shown that kairoline and γ-dimethylaminopropylbenzene are the products of the reduction (this vol., i, 421). It was recognised, however, that a rupture of the ring

between the nitrogen atom and the methylene chain might be possible under suitable conditions, and it is now found that 1:1-dimethyldihydroindolium chloride suffers reduction in all three possible ways, one being in the above sense, thus:

$$C_6H_4<\overset{CH_2}{\underset{\underset{Cl}{|}}{NMe_2}}>CH_2 \rightarrow C_6H_4<\overset{CH_2}{\underset{NMe}{}}>CH_2 \text{ (I.)}$$

$$\text{and } \begin{cases} CH_2Ph\cdot CH_2\cdot NMe_2 & \text{(II)} \\ C_6H_4Et\cdot NMe_2 & \text{(III)}. \end{cases}$$

The total yield of reduction products is about 90%, and of the mixture, 75% is the base (I), 8% is the base (II), and 17% the base (III).

1:1-*Dimethyldihydroindolium iodide*, m. p. 195—196°, was prepared from the readily obtainable 1-methyldihydroindole, and this was converted into a solution of the chloride and treated with sodium amalgam. The mixture of the three bases separated as a brown oil, which was digested for several hours with formaldehyde and hydrochloric acid at 100°. The product was then rendered alkaline and distilled in a current of steam, whereby the 1-methyldihydroindole was left behind as the di-indylmethane derivative, $CH_2\left(C_6H_3<\overset{CH_2}{\underset{NMe}{}}>CH_2\right)_2$. The volatile oil was next treated with methyl iodide at 0°, whereby (II) was converted into the known β-phenylethyltrimethylammonium iodide,

$$CH_2Ph\cdot CH_2\cdot NMe_3I,$$

which yielded styrene on distillation with silver oxide. The remaining *dimethyl-o-ethylaniline*, (III), was left unchanged. It has b. p. 196—197°/747 mm., and forms a salmon-coloured *platinichloride*, decomp. 273—275°, and a *picrate*, m. p. 145°, and reacts very sluggishly with methyl iodide to give the *methiodide*, m. p. 162—164°. J. C. W.

Preparation and Properties of the α-Halogen Derivatives of Quinoline and Methylquinoline. II. O. FISCHER and HEINRICH GUTHMANN (*J. pr. Chem.*, 1916, [ii], **93**, 378—386).—As an improvement on the method described earlier (Fischer, A., 1898, i, 382) for the conversion of quinolones into the corresponding chloroquinoline compounds by heating with phosphorus pentachloride, using phosphoryl chloride as solvent, it is recommended that the last substance be replaced by *p*-dichlorobenzene, and that *p*-dibromobenzene be used for a similar purpose in treating with phosphorus pentabromide. Even the crude mixture of the isomerides may be used in place of the pure para-compound, and the advantages gained include the possibility of working in open vessels, the greater solvent power of the medium, and the ease with which this can be removed by steam distillation or extraction.

The following compounds were prepared by the modified process: 2-chloroquinoline from 1-methyl-2-quinolone; 2-chloro-6-methylquinoline and 2-*bromo*-6-*methylquinoline*, prismatic columns, m. p. 126° (*mercurichloride*, needles, m. p. 169°), from 1:6-dimethyl-

2-quinolone; 2-*chloro*-6-*nitroquinoline*, m. p. 235°, from 6-nitro-1-methyl-2-quinolone, the product yielding a substance, m. p. 280°, probably 6-nitro-2-hydroxyquinoline when heated with hydrochloric acid.

It was found that of the 2-chloro-5-nitro-, 2-chloro-6-nitro-, and 2-chloro-8-nitro-quinolines, the 2-chloro-6-nitro-compound was less reactive towards concentrated aqueous ammonia solution, requiring twenty hours at 150°, whereas its isomerides named needed only ten and seven hours respectively. The products respectively were: 5-*nitro*-2-*aminoquinoline*, orange-coloured prisms, m. p. 239°; 6-*nitro*-2-*aminoquinoline*, yellow prisms, m. p. 265°; and 8-*nitro*-2-*aminoquinoline*, stout, yellow crystals, m. p. 159°; orange-coloured *picrate*, m. p. 257°; *mercurichloride*, yellow, crystalline powder, m. p. 216°; *acetyl* derivative, colourless needles, m. p. 211°; *benzoyl* derivative, colourless, broad needles, m. p. 166°.

D. F. T.

Chromoisomerism of Onium-compounds. II. "Chromoisomerism" of the Salts of 9-Phenylacridine. F. KEHRMANN and A. DANECKI (*Ber.*, 1916, **49**, 1338—1341).—One of Hantzsch's examples of so-called chromoisomeric salts is found in the case of 9-phenylacridine, of which yellow, green, and red sulphates, green, brown, and reddish-brown chlorides, etc., have been described. It is now shown that all these colours are due to a slight impurity in the base. When a solution in dilute sulphuric acid is boiled with animal charcoal for some time and the base is reprecipitated and crystallised from alcohol, it is obtained in long, very pale yellow, pointed prisms, m. p. 184°. The pure base forms salts of only one colour, for example, a yellow sulphate, but different crystalline forms are observed according to the temperature, concentration, and acidity of the solution from which they separate. It is remarkable that the impurity should colour the two forms, especially in the case of the sulphate, in almost complementary shades.

J. C. W.

Arylamides of Thiocyanoacetic Acid and Aryl-ψ-thiohydantoins. H. BECKURTS and G. FRERICHS (*Arch. Pharm.*, 1915, **253**, 233—265).—Chloroacetoarylamides, $CH_2Cl{\cdot}CO{\cdot}NHAr$, which are readily obtained from chloroacetyl chloride and the aromatic amine in benzene solution, react with potassium thiocyanate in the presence of alcohol to form generally the thiocyanoacetoarylamide, $NHAr{\cdot}CO{\cdot}CH_2{\cdot}SCN$; in a few cases the thiocarbimido-compound, $NHAr{\cdot}CO{\cdot}CH_2{\cdot}NCS$, is obtained, but it cannot be purified as it changes so rapidly into the isomeric thiocyano-compound. The latter, by prolonged heating with water or, in the case of the sparingly soluble members, with glacial acetic acid, are converted into aryl-ψ-thiohydantoins. These form crystalline salts with hydrogen chloride and also with sodium hydroxide by direct addition, and are converted into 2:4-diketo-3-aryltetrahydrothiazoles, $S<\begin{matrix}CO-NAr\\ CH_2{\cdot}CO\end{matrix}$, by prolonged heating with 25% hydrochloric acid in a sealed tube at 100°.

The following compounds have been prepared: *chloroaceto*-m-*toluidide*, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4Me$, small, colourless prisms, m. p. 90—91°; *thiocarbimidoaceto*-m-*toluidide*,

$$C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot NCS,$$

leafy crystals, m. p. 99°; *thiocyanoaceto*-m-*toluidide*,

$$C_6H_4Me\cdot NH\cdot CO\cdot CH_2\cdot SCN,$$

microscopic, faintly yellow crystals, m. p. 136°; 3-m-*tolyl-ψ-thiohydantoin*, $CH_2<\begin{matrix}CO\cdot N\cdot C_6H_4Me\\ SC:NH\end{matrix}$, colourless, microscopic, quadratic leaflets, m. p. 161°, which forms a *hydrochloride*, $C_{10}H_{10}ON_2S,HCl$, and a *compound* with sodium hydroxide (5% aqueous solution), $C_{10}H_{10}ON_2S,NaOH,4H_2O$, colourless leaflets, from which, by heating with ethyl iodide and alcohol in a sealed tube at 100°, is obtained 3-m-*tolyl-ω-ethyl-ψ-thiohydantoin*, $CH_2<\begin{matrix}CO\cdot N\cdot C_6H_4Me\\ SC:NEt\end{matrix}$, colourless, microcrystalline powder, m. p. 106—107°; 2:4-*diketo*-3-m-*tolyltetrahydrothiazole*, $S<\begin{matrix}CO-N\cdot C_6H_4Me\\ CH_2\cdot CO\end{matrix}$, colourless needles, m. p. 90—91°.

From *chloroaceto-ψ-cumidide*, $C_{11}H_{14}ONCl$, colourless needles, m. p. 159°, is obtained the series *thiocyanoaceto-ψ-cumidide*, $C_{12}H_{14}ON_2S$, small, yellowish-white crystals, m. p. 105°; 3-*ψ-cumyl-ψ-thiohydantoin*, $C_{12}H_{14}ON_2S$, faintly yellow prisms, m. p. 210° (*hydrochloride*; sodium hydroxide *compound*,

$$C_{12}H_{14}ON_2S,NaOH,5H_2O,$$

colourless needles; 3-*ψ-cumyl-ω-ethyl-ψ-thiohydantoin*, $C_{14}H_{18}ON_2S$, faintly yellow prisms, m. p. 138°).

Chloroaceto-p-*chloroanilide*, $C_8H_7ONCl_2$, colourless needles, m. p. 169°, yields p-*chlorothiocarbimidoacetanilide*, which could not be isolated; p-*chlorothiocyanoacetanilide*, $C_9H_7ON_2ClS$, microcrystalline needles, m. p. 126°; 3-p-*chlorophenyl-ψ-thiohydantoin*, $C_9H_7ON_2ClS$, colourless needles, m. p. 213° (*hydrochloride*, $C_9H_7ON_2ClS,HCl$, oblong, microscopic leaflets; sodium hydroxide *compound*, $C_9H_7ON_2ClS,NaOH,5H_2O$, large, brown prisms; 3-p-*chlorophenyl-ω-ethyl-ψ-thiohydantoin*, $C_{10}H_{11}ON_2ClS$, colourless, microscopic needles, m. p. 106—107°); and 2:4-*diketo*-3-p-*chlorophenyltetrahydrothiazole*, $C_9H_6O_2NClS$, colourless needles, m. p. 145°.

Chloroaceto-m-*chloroanilide*, stout, colourless leaflets, m. p. 101°, yields m-*chlorothiocyanoacetanilide*, microscopic prisms, m. p. 165—166°; 3-m-*chlorophenyl-ψ-thiohydantoin*, tufts of colourless needles, m. p. 180—181° (*hydrochloride* with 1HCl, faintly yellow, oblong crystals; sodium hydroxide *compound*, reddish-brown powder with $4\frac{1}{2}H_2O$); and 2:4-*diketo*-3-m-*chlorophenyltetrahydrothiazole*, yellow needles, m. p. 116—117°.

o-*Nitrochloroacetanilide*, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot NO_2$, pale yellow needles, m. p. 88°, yields o-*nitrothiocyanoacetanilide*, $C_9H_7O_3N_3S$, crystalline powder, m. p. 154°; 3-o-*nitrophenyl-ψ-thiohydantoin*, $C_9H_7O_3N_3S$, almost colourless, microscopic plates, m. p. 172° (sodium hydroxide *compound*, intensely yellow needles with $3H_2O$;

3-o-*nitrophenyl-ω-ethyl-ψ-thiohydantoin*, $C_{11}H_{11}O_3N_3S$, pale brown, viscous oil).

m-*Nitrochloroacetanilide*, almost colourless leaflets, m. p. 114°, yields m-*nitrothiocyanoacetanilide*, small, yellow needles, m. p. 180°; 3-m-*nitrophenyl-ψ-thiohydantoin*, pale yellow, microscopic needles, m. p. 199° (sodium hydroxide *compound*, yellowish-brown, microcrystalline powder with $2H_2O$; 3-m-*nitrophenyl-ω-ethyl-ψ-thiohydantoin*).

p-*Nitrochloroacetanilide*, yellowish-white leaflets, m. p. 182°, yields p-*nitrothiocyanoacetanilide*, pale yellow needles, m. p. 174°; 3-p-*nitrophenyl-ψ-thiohydantoin*, pale yellow, microscopic, oblong plates, m. p. 245° (sodium hydroxide *compound*, yellow needles with $4H_2O$; 3-p-*nitrophenyl-ω-ethyl-ψ-thiohydantoin*, small, yellow needles, m. p. 129°).

3-*Nitrochloroaceto*-p-*toluidide*, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}C_6H_3Me{\cdot}NO_2$, yellow needles, m. p. 119°, prepared from 3-nitro-*p*-toluidine and chloroacetyl chloride or by treating chloroaceto-*p*-toluidide with nitric acid (D 1·41), yields 3-*nitrothiocyanoaceto*-p-*toluidide*, $C_{10}H_9O_3N_3S$, almost colourless needles, m. p. 133°; 3-m-*nitro*-p-*tolyl-ψ-thiohydantoin*, pale brown prisms or pale yellow, microcrystalline powder, m. p. 185° (sodium hydroxide *compound*, yellow, microscopic crystals with $3H_2O$; 3-m-*nitro*-p-*tolyl-ω-ethyl-ψ-thiohydantoin*, pale brown oil).

2-*Nitrochloroaceto*-p-*toluidide*, pale yellow prisms, m. p. 129°, yields 2-*nitrothiocyanoaceto*-p-*toluidide*, microscopic, quadratic leaflets, m. p. 184°; 3-o-*nitro*-p-*tolyl-ψ-thiohydantoin*, colourless prisms, m. p. 206—207° (sodium hydroxide *compound*, yellow, microscopic leaflets with $2H_2O$; 3-o-*nitro*-p-*tolyl-ω-ethyl-ψ-thiohydantoin*, small, yellow leaflets, m. p. 142°).

5-*Nitrochloroaceto*-o-*toluidide*, pale yellow needles, m. p. 122°, yields 5-*nitrothiocyanoaceto*-o-*toluidide*, colourless, microscopic prisms, m. p. 158°; 3-5′-*nitro*-o-*tolyl-ψ-thiohydantoin*, yellow, microscopic, rhombic leaflets, m. p. 172° (sodium hydroxide *compound*, yellow, microscopic needles with $3H_2O$; 3-5′-*nitro*-o-*tolyl-ω-ethyl-ψ-thiohydantoin*, yellow, microscopic, rhombic leaflets, m. p. 127—128°).

Chloroaceto-p-*anisidide*, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}OMe$, colourless prisms, m. p. 122°, yields *thiocarbimidoaceto*-p-*anisidide*,

$$OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NCS,$$

faintly red leaflets (impure); *thiocyanoaceto*-p-*anisidide*,

$$OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}SCN,$$

faintly yellow prisms, m. p. 110—111°; 3-p-*anisyl-ψ-thiohydantoin*, colourless leaflets rapidly becoming yellowish-brown, m. p. 184° (*hydrochloride*, yellow leaflets; sodium hydroxide *compound*, yellowish-white leaflets with $4H_2O$; 3-p-*anisyl-ω-ethyl-ψ-thiohydantoin*, colourless prisms, m. p. 84—85°); and 2:4-*diketo*-3-p-*anisyltetrahydrothiazole*, colourless needles, m. p. 166°.

Chloroaceto-o-*anisidide*, colourless needles or rhombic plates, m. p. 51°, yields *thiocyanoaceto*-o-*anisidide*, colourless prisms, m. p. 72°; 3-o-*anisyl-ψ-thiohydantoin*, yellow prisms, m. p. 149°, crystals with $1C_2H_4O_2$, m. p. 110—111° (*hydrochloride*; sodium hydroxide

compound, colourless needles with $4H_2O$; 3-o-*anisyl-ω-ethyl-ψ-thiohydantoin*, yellow, rhombic plates, m. p. 126—127°); and 2:4-*diketo*-3-o-*anisyltetrahydrothiazole*, yellow, rhombic plates, m. p. 113—114°.

Thiocyanoaceto-p-*phenetidide*, almost colourless, microscopic prisms, m. p. 130—131°, changes very readily in glacial acetic acid into 3-p-*phenetyl-ψ-thiohydantoin*, m. p. 167° (Grothe, who described the compound as thiocyanoaceto-*p*-phenetidide, gave 164°), which forms a *hydrochloride*, faintly yellow, microscopic needles, and a sodium hydroxide *compound*, yellowish-white prisms with $4H_2O$. 3-p-*Phenetyl-ω-ethyl-ψ-thiohydantoin*, m. p. 94—95°, forms yellowish-brown, rhombic plates, and 2:4-*diketo*-3-p-*phenetyltetrahydrothiazole*, m. p. 155—156°, small, yellow needles. C. S.

New Derivatives of Benzthiazole and its Homologues. BERTHOLD RASSOW, WILHELM DÖHLE, and EDWIN REIM (*J. pr. Chem.*, 1916, [ii], **93**, 183—184).—Hoffmann (*Diss.*, Leipzig, 1912) has shown that phenylthiolacetic acid is converted by sulphur sesquioxide into red dyes of the "thioindigo" group. Since dehydrothiotoluidine (2-*p*-aminophenyl-5-methylbenzthiazole) is converted by sulphur sesquioxide into a yellow sulphur dye, the authors have examined the behaviour of benzthiazole and of 3- and 5-methylbenzthiazoles towards the same reagent (compare following abstracts). C. S.

New Derivatives of Benzthiazole. B. RASSOW and W. DÖHLE (*J. pr. Chem.*, 1916, [ii], **93**, 184—213).—The reaction between benzthiazole and sulphur sesquioxide yields yellow, insoluble substances, which do not exhibit the character of vat-dyes, and cannot be separated from admixed sulphur; they have therefore not been further examined. The benzthiazole is mainly converted into sulphonic acids.

In 1888 Möhlau and Krohn obtained benzthiazole and a substance, $C_8H_7NS_2$, by heating dimethylaniline with sulphur. The authors have employed the same method, and have obtained, in addition to the two compounds mentioned, three other substances, one of which, crystals, m. p. 265°, was obtained in a quantity too small to admit of examination, whilst the other two proved to be 1-anilinobenzthiazole and 1-thiolbenzthiazole respectively. When iodine is used as a catalyst in the reaction, almost the only products are asphalt-like substances of high molecular weight.

When heated with fuming sulphuric acid (25% SO_3) at 100°, benzthiazole yields a mixture of three monosulphonic acids; the sulpho-groups have been introduced into positions 3, 5, and 6 respectively. *Benzthiazole*-6-*sulphonic acid*, $C_7H_4NS{\cdot}SO_3H,\frac{1}{2}H_2O$, forms flattened prisms, the 3-*sulphonic acid* highly refractive prisms, and the 5-*sulphonic acid* flattened prisms; they are all strong acids, and have no m. p. When their potassium salts are boiled with alcoholic potassium hydroxide, the solutions, after acidification, yield formic acid, and 3-*amino*-2-*thiolbenzenesulphonic acid*,

$NH_2\cdot C_6H_3(SH)\cdot SO_3H$, long, slender needles; *2-amino-3-thiolbenzenesulphonic acid*, short prisms; and *4-amino-3-thiolbenzenesulphonic acid*, sparingly soluble needles, which are converted into the three anilinesulphonic acids by heating with hydriodic acid (D 1·7) and phosphorus at 110—120° in a sealed tube. On diazotisation, the three aminothiolbenzenesulphonic acids yield, not diazo-sulphides, but true diazonium compounds, which are very unstable, but can be coupled with β-naphthol, producing azo-dyes, which develop a red shade on wool in a neutral bath.

The substance $C_8H_7NS_2$ obtained by Möhlau and Krohn, and to which they ascribed the formula $C_6H_4<\begin{matrix}—N—CH_2\\ \quad | \quad\ \ |\\ S\cdot CH.S\end{matrix}$, is called benzthiazolemethene sulphide by the present authors, who advance evidence in favour of this constitution. The substance forms a *methiodide*, $C_8H_7NS_2,MeI$, crystals, m. p. 139°, and *ethiodide*, m. p. 132°, yields *o*-thiolmonomethylaniline by fusion with potassium hydroxide at 200—230°, and readily yields one-half of its sulphur in the form of lead sulphide when boiled with *N*-sodium hydroxide and lead acetate. When oxidised with moderately concentrated nitric acid (2 : 1) at 0—10°, it yields Möhlau, Krohn, and Klopfer's 1 : 2-methylenebenzthiazole and also a *substance*, $C_{16}H_{18}O_2N_2S_2$, plates, m. p. 107—108°, which is soluble in 35% hydrochloric acid, forms a *periodide*, $C_{16}H_{14}O_2N_2S_2I_4$, concentric needles, m. p. 150—151°, yields formic acid, methylaniline, and *o*-thiolmonomethylaniline by fusion with potassium hydroxide, and appears to be a disulphide, $S_2(C_6H_4\cdot NMe\cdot CHO)_2$. 1 : 2-Methylenebenzthiazole forms an unstable *methiodide*, is not attacked by hydriodic acid and phosphorus, and by fusion with potassium hydroxide or by boiling with concentrated aqueous barium hydroxide yields formic acid and *o*-thiolmonomethylaniline.

By heating at 120° with ten times its weight of fuming sulphuric acid (25% SO_3), benzthiazolemethylene sulphide yields a *sulphonic acid*, $C_8H_6NS_2\cdot SO_3H$, colourless needles, m. p. 134°, which is very hygroscopic and the salts of which are stable, crystalline substances except the *mercuric* salt; this is a jelly, which presents striking analogies to true organic jellies such as gelatin and agar-agar. By boiling its barium salt with aqueous barium hydroxide the sulphonic acid is decomposed into carbon dioxide, hydrogen sulphide (in amount equivalent to 1 atom of sulphur), and *4-methylamino-3-thiolbenzenesulphonic acid*, $NHMe\cdot C_6H_3(SH)\cdot SO_3H$, colourless needles, decomp. 237°. The last compound is converted into the corresponding *disulphide*, yellow needles, by repeated evaporation of its aqueous solution, and is reduced by boiling hydriodic acid (D 1·7) and phosphorus, yielding hydrogen sulphide and a *methylaminobenzenesulphonic acid*, $NHMe\cdot C_6H_4\cdot SO_3H$, decomp. 244°, which does not agree in its properties with any one of the four acids described in the literature; it should be the para-derivative, since it yields *p*-benzoquinone by oxidation with chromic acid.

By careful oxidation with nitric acid, D 1·4, the sulphonic acid of benzthiazolemethene sulphide yields sulphuric acid and two other substances, one of which, $C_8H_7O_3NS_2$, needles, appears to be

1 : 2-*methylenebenzthiazolesulphonic acid*, $SO_3H\cdot C_6H_3<\begin{matrix}-N-\\ S\cdot CH\end{matrix}>CH_2$ and the other, $C_8H_5O_2NS_2$, prisms, its anhydride; these two are convertible the one into the other. C. S.

New Derivatives of 3- and 5-Methyl-benzthiazoles. BERTHOLD RASSOW and EDWIN REIM (*J. pr. Chem.*, 1916, [ii], **93**, 214—253. Compare preceding abstracts).—The reaction between sulphur and dimethyl-*o*- and -*p*-toluidines has been examined to ascertain whether products analogous to those formed in the case of dimethylaniline are obtained.

By boiling a mixture of sulphur and dimethyl-*o*-toluidine, a considerable amount of *o*-toluidine is obtained, together with a little 3-methylbenzthiazole (about 3%), *s*-di-*o*-tolylthiocarbamide, and a large amount of tar. 3-*Methylbenzthiazole*, $C_6H_3Me<\begin{matrix}N\\ S\end{matrix}>CH$, colourless liquid, b. p. 252—253°, is a weak base; the *hydrochloride*, needles; *picrate*, rhombic leaflets; *platinichloride*, long, yellow needles; *aurichloride*, needles; *ferrocyanide*, pale green leaflets; *zincichloride*, rhombic prisms; *mercurichloride*, leaflets; and *methiodide*, m. p. about 201—203°, colourless needles (obtained in very small quantity, owing to steric influence), have been prepared. The base yields formic acid and 3-thiol-*o*-toluidine by fusion with potassium hydroxide, and is sulphonated by fuming sulphuric acid (25% SO_3) on the water-bath, yielding a *monosulphonic acid*, $C_8H_7O_3NS_2,H_2O$, prismatic needles, of which the salts other than the *silver* and *barium* salts are easily soluble in water.

Dimethyl-*p*-toluidine and sulphur under the same conditions yield considerable quantities of carbon disulphide, hydrogen sulphide, and *p*-toluidine, and only small amounts of 5-methylbenzthiazole and of the corresponding methylene sulphide. 5-Methylbenzthiazole forms a *mercurichloride*, $C_8H_7NS,HgCl_2$, needles, m. p. 193—194° (decomp.), and a *methiodide*, leaflets, m. p. about 198—204°, yields formic acid and 3-thiol-*p*-toluidine by fusion with potassium hydroxide, and is converted into a *monosulphonic acid*, $C_8H_7O_3NS_2$, rhombic prisms, by fuming sulphuric acid at 100°. 5-*Methylbenzthiazolemethylene sulphide*, $C_6H_3Me<\begin{matrix}-N-CH_2\\ S\cdot CH\cdot S\end{matrix}$ colourless prisms, m. p. 134°, distils without decomposition, is so weak a base that its salts cannot be isolated, forms a *methiodide*, $C_9H_9NS_2,MeI$, faintly yellow prisms (decomposing into its components at 150°), and *periodide*, $C_9H_9NI_2S_2$, reddish-brown leaflets, yields carbon dioxide, hydrogen sulphide, and 3-thiolmethyl-*p*-toluidine by fusion with potassium hydroxide, is converted by bromine water into a *substance*, C_9H_9ONS, colourless crystals, m. p. 78°, and is easily sulphonated by fuming sulphuric acid at 100°, a *sulphonic acid*, $C_9H_8NS_2\cdot SO_3H,2H_2O$, almost colourless crystals, being formed, the purification of which is troublesome. This sulphonic acid is converted by nitric acid (D 1·4) on the water-bath into 5-methyl-1 : 2-methylenebenzthiazolesulphonic acid (see below).

When oxidised with dilute nitric acid on the water-bath, 5-methylbenzthiazolemethylene sulphide yields, in addition to a very small quantity of 5 : 5′-*dimethyl*-1 : 1′-*dibenzthiazole*,

$$C_6H_3Me<{}^{N}_{S}>C\cdot C<{}^{N}_{S}>C_6H_3Me,$$

faintly yellow leaflets, m. p. 270°, the *hydrogen sulphate*, colourless prisms, m. p. 203—204°, of 5-*methyl*-1 : 2-*methylenebenzthiazole*, to which is ascribed the formula $C_6H_3Me<{}^{-N-}_{S\cdot CH}>CH_2$, analogous to that of the corresponding benzene derivative (preceding abstract). The base is very difficult to isolate on account of its oxidisability and lack of crystallising power, but from the hydrogen sulphate the *hydrochloride*, C_9H_9NS,HCl,H_2O, prisms, has been prepared; this salt is neutral to litmus and to methyl-orange. When titrated, however, with phenolphthalein as indicator, both the hydrochloride and the hydrogen sulphate neutralise one equivalent of alkali more than corresponds with the theoretical amount. By evaporating an aqueous solution of the hydrogen sulphate and sodium hydroxide (3 equiv.) to dryness, a *sodium* salt,

$$C_9H_{10}ONSNa,H_2O,$$

rhombic leaflets, is obtained, which is regarded as the sodium salt of 3-*thiolformylmethyl*-p-*toluidide*, $SNa\cdot C_6H_3Me\cdot NMe\cdot CHO$. An aqueous solution of this salt yields, by atmospheric oxidation, a *disulphide*, $S_2(C_6H_3Me\cdot NMe\cdot CHO)_2$, colourless crystals, which is converted by successive treatment with sodium amalgam and hydrochloric acid into 5-methyl-1 : 2-methylenebenzthiazole hydrochloride. The preceding hydrogen sulphate, by treatment with hot aqueous barium hydroxide and then with barium permanganate, is converted by oxidation of the intermediate thiol compound into *barium formylmethyl*-p-*toluidide*-3-*sulphonate*, $(C_9H_{10}O_4NS)_2Ba$, the aqueous solution of which, heated on the water-bath with dilute sulphuric acid, yields formic acid and *methyl*-p-*toluidine*-3-*sulphonic acid*, $SO_3H\cdot C_6H_3Me\cdot NHMe$, colourless prisms.

The 5-methyl-1 : 2-methylenebenzthiazolesulphonic acid mentioned above is obtained in better yield by heating the hydrogen sulphate or hydrochloride of 5-methyl-1 : 2-methylenebenzthiazole (or the sodium salt of the formyl derivative) with fuming sulphuric acid on the water-bath. It crystallises in rhombic prisms, is not decomposed at 250°, dissolves in alkalis and in concentrated acids, but has a neutral reaction to litmus and methyl-orange. It forms a *mercurichloride*, $C_9H_9O_3NS_2,HgCl_2$, needles, and a *potassium* salt, $C_9H_7O_3NS_2K_2,2H_2O$ (which retains its water at 160° and is regarded as having the constitution

$$CHO\cdot NMe\cdot C_6H_2Me[SK]\cdot SO_3K,H_2O),$$

yields a *nitro*-compound, $C_9H_8O_5N_2S_2$, yellow needles, by nitration, and is oxidised by barium permanganate and carbonate to *barium formylmethyl*-p-*toluidide*-2 : 3-*disulphonate*, $C_9H_9O_7NS_2Ba,2H_2O$, colourless, prismatic needles. The free disulphonic acid cannot

be obtained, since it is decomposed by water into formic and sulphuric acids and *methyl*-p-*toluidine-2-sulphonic acid*,

$$SO_3H\cdot C_6H_3Me\cdot NHMe,$$

colourless leaflets (*sodium* salt, colourless leaflets with $1H_2O$).

C. S.

Reactions of the Formamidines. VI. Some Thiazole Derivatives. F. B. DAINS and A. E. STEPHENSON (*J. Amer. Chem. Soc.*, 1916, **38**, 1841—1844).—In earlier papers (A., 1902, i, 602; 1909, i, 781; 1913, i, 1086, 1096) it has been shown that compounds containing a methylene group react with substituted formamidines, thus: $CH_2XY + NR{:}CH\cdot NHR = CXY{:}CH\cdot NHR + NH_2R$. The investigation has now been extended to the reaction of ψ-thiohydantoins (tetrahydrothiazolones) with formamidines.

When diphenyl-ψ-thiohydantoin [2-phenylimino-3-phenyltetrahydrothiazole-4-one] is heated with diphenylformamidine at 140—150°, *2-phenylimino-3-phenyl-5-anilinomethylenetetrahydrothiazole-4-one*, $NPh{:}C{<}{\begin{array}{l}NPh\cdot CO\\ S\text{——}C{:}CH\cdot NHPh\end{array}}$, m. p. 202°, is produced, which forms short, pale yellow needles, and on hydrolysis with hydrochloric acid yields diphenylcarbamide, 3-phenyl-5-anilinomethylenetetrahydrothiazole-2:4-dione (m. p. 192°), 3-phenyltetrahydrothiazole-2:4-dione, and aniline hydrochloride.

2:3-Di-*o*-tolyl-ψ-thiohydantoin (Wheeler and Jamieson, A., 1903, i, 522) has m. p. 153°, and its benzylidene derivative, m. p. 182·5°. When this ψ-thiohydantoin is heated with diphenylformamidine, *2-*o*-tolylimino-3-*o*-tolyl-5-anilinomethylenetetrahydrothiazole-4-one*, m. p. 200—201°, is produced, which crystallises in pale yellow, silky needles.

Phenyl-ψ-thiohydantoin reacts with diphenylformamidine with formation of *2-phenylimino-5-anilinomethylenetetrahydrothiazole-4-one*, $NPh{:}C{<}{\begin{array}{l}NH\cdot CO\\ S\text{——}C{:}CH\cdot NHPh\end{array}}$, m. p. 266·5°, which forms lemon-yellow needles. This compound can also be obtained by the interaction of phenyl*iso*thiohydantoic acid with diphenylformamidine; an analogous ring-formation takes place when phenyl*iso*thiohydantoic acid is heated with benzaldehyde, 2-phenylimino-5-benzylidenetetrahydrothiazole-4-one (Wheeler and Jamieson, A., 1903, i, 521) being produced.

2-Phenylmethylaminotetrahydrothiazole-4-one condenses with diphenylformamidine with production of *2-phenylmethylamino-5-anilinomethylenetetrahydrothiazole-4-one*,

$$NPhMe\cdot C{\ll}{\begin{array}{l}N\cdot CO\\ S\text{--}C{:}CH\cdot NHPh\end{array}},$$

m. p. 180°, which crystallises in red granules.

When 3-phenyltetrahydrothiazole-2:4-dione is heated with diphenylformamidine, *3-phenyl-5-anilinomethylenetetrahydrothiazole-2:4-dione*, m. p. 192—193°, is formed, which crystallises in lustrous pale yellow leaflets.

By the interaction of diphenylformamidine and tetrahydrothiazole-2:4-dione, 5-*anilinomethylenetetrahydrothiazole*-2:4-*dione*, $CO<\begin{matrix}NH\cdot CO\\ S\text{—}\overset{|}{C}:CH\cdot NHPh\end{matrix}$, m. p. 233°, is produced, which forms nearly colourless plates. E. G.

Heterocyclic Sulphones. IV. Action of Halogen Compounds on Sulphurylindoxyl. M. CLAASZ (*Ber.*, 1916, **49**, 1408—1415. Compare this vol., i, 425).—In the earlier paper on sulphurylindoxyl (benzsulphonazoline) the substance was thought to be devoid of basic properties. If, however, a solution in glacial acetic acid is saturated with hydrogen chloride, an unstable *hydrochloride*, m. p. 172° (decomp.), is deposited. It was therefore expected that reactions with halogen compounds would take place at the imino-group rather than at the methylene group, which has already been shown to be reactive. This is not exactly the case, however, for the only products which can be isolated in most instances are substituted methylene derivatives. Still, in the case of very reactive agents, there are indications that ammonium salts are first formed, which undergo further rearrangement when treated with alkalis or heated under pressure, thus:

$$C_6H_4<{NH \atop SO_2}>CH_2 \xrightarrow{+RCl} C_6H_4<{NHR\cdot Cl \atop SO_2}>CH_2 \longrightarrow$$

$$C_6H_4<{NHR \atop SO_2-}>CH \longrightarrow C_6H_4<{NH \atop SO_2}>CHR.$$

Sulphurylindoxyl reacts with benzoyl chloride in the presence of dilute sodium hydroxide to form *sulphurylindoxyl phenyl ketone* (2-*benzoylbenzsulphonazoline*), $C_6H_4<{NH \atop SO_2}>CHBz$, which crystallises in stout prisms, m. p. 124—125°. *Sulphurylindoxyl methyl ketone* (2-*acetylbenzsulphonazoline*) is obtained in glistening leaflets, m. p. 144—145°, by heating the reagents together in benzene solution. Both ketones dissolve in alkali hydroxides, but are reprecipitated by carbon dioxide, an indication of the possibility of the $-SO_2-\overset{|}{C}{=}C(OH)-$ grouping. Ethyl chloroformate also reacts in boiling benzene solution to form *ethyl sulphurylindoxylcarboxylate* (2-*carbethoxybenzsulphonazoline*), $C_6H_4<{NH \atop SO_2}>CH\cdot CO_2Et$, in glistening leaflets, m. p. 134—135°; the intermediate ammonium salt separates as the benzene solution cools, but this is decomposed by dilute sodium carbonate. Methyl iodide reacts at 120°, forming *a-methylsulphurylindoxyl* (2-*methylbenzsulphonazoline*) in colourless needles, m. p. 102°.

Ethylphenylcarbamyl chloride also reacts at 120—130°, but the expected anilide, $C_6H_4<{NH \atop SO_2}>CH\cdot CO\cdot NPhEt$, is not formed. Ap-

parently, it is hydrolysed by the liberated hydrogen chloride, and the product is *di-sulphurylindoxyl ketone*,

$$\left(C_6H_4{<}\substack{NH\\SO_2}{>}CH\right)_2CO,$$

which crystallises in stout needles, m. p. 247°.

When isatin is warmed with phosphorus pentachloride and benzene and the solution is added to sulphurylindoxyl, the compound, "*isatosulphurylindoxyl*" (I), separates as a brown precipitate, which gives a blue solution in 10% sodium hydroxide (II), from which carbon dioxide precipitates the isomeric "*sulphurylindoxyl-α-indolindigo*" (III) as a brick-red powder, m. p. 171—172°:

$$\underset{\text{(I.)}}{C_6H_4{<}\substack{NH\\SO_2}{>}CH\cdot C{\lessdot}\substack{N-\\CO}{>}C_6H_4} \longrightarrow \underset{\text{(II.)}}{{>}CH\cdot \overset{NaO}{\overset{|}{C}}{<}\substack{NH\cdot\\CO}} \longrightarrow$$

$$\underset{\text{(III.)}}{C_6H_4{<}\substack{NH\\SO_2}{>}C{=}C{<}\substack{NH\\CO}{>}C_6H_4.}$$

J. C. W.

Products Formed by the Addition of Methyl Iodide to the Diphenylethylthiocarbamides. ERIK OHLSSON (*Ber.*, 1916, **49**, 1341—1344).—The diphenylethylthiocarbamides (A., 1914, i, 830) quickly combine with methyl iodide on warming, to form the hydriodides of the methyl phenylethyliminophenylethylthiocarbamates, thus:

$$CS[NH\cdot CHPhMe]_2 + MeI = CHPhMe\cdot N{:}C(SMe)\cdot NH\cdot CHPhMe,HI.$$

The free bases are remarkably stable.

l-Di-α-phenylethylthiocarbamide yields *methyl* l-*α-phenylethylimino-α-phenylethylthiocarbamate*, m. p. 68°, $[\alpha]_D$ +96°; *hydriodide*, m. p. 144°, $[\alpha]_D$ +138°; *hydrochloride*, m. p. 149·5°, $[\alpha]_D$ +193°. The d-*ester* has similar characteristics. The *racemic ester*, from the mixed esters, crystallises in long prisms, m. p. 88°; *hydriodide*, from the racemic carbamide, m. p. 121°; *hydrochloride*, m. p. 126°. The *meso-ester* has m. p. 39°, and its *hydriodide*, m. p. 86°.

The esters are decomposed into methyl mercaptan and diphenylethylcarbamides on heating with aqueous alcohol for some hours, thus:

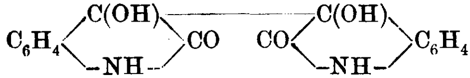
$$CHPhMe\cdot N{:}C(SMe)\cdot NH\cdot CHPhMe + H_2O = MeSH + CO[NH\cdot CHPhMe]_2.$$

d-*Di-α-phenylethylcarbamide* crystallises in long, slender needles, m. p. 210°, $[\alpha]_D$ +59°; the l-*compound* also has m. p. 210°; the *racemic substance* has m. p. 180°; and the *meso*-form has m. p. 153°.

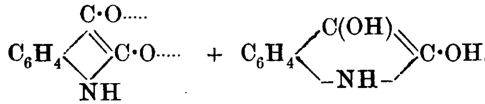
J. C. W.

Constitution of Isatide. GUSTAV HELLER (*Ber.*, 1916, **49**, 1406—1408).—Kohn and his co-workers explain the production of

a tetra-acetyl derivative of isatide by writing this as a pinacone (I) (A., 1912, i, 800; this vol., i, 607). This does not explain why the compound should be so easily decomposed by alkalis, and the alternative formula (II) is proposed, which also indicates why the quinhydrone is colourless. It is based on Pfeiffer's theories (A., 1914, i, 551):



(I.)



(II.)

J. C. W.

Pyrimidines. LXXXI. Secondary Pyrimidine-Nucleosides and their Unique Behaviour on Hydrolysis. TREAT B. JOHNSON and SIDNEY E. HADLEY (*J. Amer. Chem. Soc.*, 1916, **38**, 1844—1853).—This paper gives an account of a continuation of work on compounds of uracil and thymine containing alcohol groups in the 4-position of the pyrimidine ring (Johnson and Chernoff, A., 1913, i, 656; 1914, i, 1091). The terms primary, secondary, and tertiary are applied to compounds containing respectively the typical alcohol groups, $\cdot CH_2\cdot OH$, $\cdot CHMe\cdot OH$, and $\cdot CMe_2\cdot OH$. The primary nucleosides of uracil and thymine have already been described, and an attempt has now been made to prepare the secondary uracil nucleoside,

$$NH<{CO\cdot NH \atop CO-CH}>C\cdot CHMe\cdot OH.$$

Ethyl γ-ethoxy-α-methylpropionylacetate,

$$OEt\cdot CHMe\cdot CO\cdot CHMe\cdot CO_2Et,$$

b. p. 114°/14 mm., was prepared by the condensation of ethyl α-ethoxypropionate with ethyl propionate in presence of sodium. This ester combines readily with thiocarbamide in presence of sodium ethoxide with formation of *2-thio-4-α-ethoxyethyltetrahydropyrimid-6-one*, $NH<{CS\cdot NH \atop CO\cdot CH}>C\cdot CHMe\cdot OEt$, m. p. 206—208°, which crystallises in stout prisms. This compound, when desulphurised with chloroacetic acid, yields *4-α-ethoxyethyltetrahydropyrimid-2:6-dione*, $NH<{CO\cdot NH \atop CO-CH}>C\cdot CHMe\cdot OEt$, m. p. 184—186°, which forms long, colourless prisms, and on bromination is converted into *5-bromo-4-α-ethoxyethyltetrahydropyrimid-2:6-dione*, $NH<{CO\cdot NH \atop CO-CBr}>C\cdot CHMe\cdot OEt$, m. p. 206°, which crystallises in flat prisms.

When 4-α-ethoxyethyltetrahydropyrimid-2:6-dione is hydrolysed

with hydrobromic or hydriodic acid, the corresponding secondary uracil-nucleoside, $NH<\begin{smallmatrix}CO\cdot NH\\CO-CH\end{smallmatrix}>C\cdot CHMe\cdot OH$, is not produced, but carbon dioxide, ethyl haloid, and a basic substance, $C_5H_8ON_2$, are formed in accordance with the equation $C_8H_{12}O_3N_2+H_2O+HBr=C_2H_5Br+CO_2+H_2O+C_5H_8ON_2$. The *compound*, $C_5H_8ON_2$, crystallises in plates or prisms, and does not melt below 300°; its constitution has not been determined. E. G.

Pyrimidines. LXXXII. Synthesis of 1 : 3-Diamines by Reduction of 2-Mercapto-6-oxypyrimidines [2-Thiodihydropyrimid-6-ones]. TREAT B. JOHNSON and A. WILLARD JOYCE (*J. Amer. Chem. Soc.*, 1916, **38**, 1854—1860).—In an earlier paper (this vol., i, 608) the authors have shown that when 6-chloro-2-thiolpyrimidines are treated with sodium and alcohol they undergo reduction with formation of 1 : 3-diamines. A study has now been made of the action of these reagents on 2-thiolpyrimid-6-ones, and it has been found that, in this case also, reduction takes place smoothly with production of the corresponding 1 : 3-diamines. This reaction renders it possible to obtain alkyl derivatives of 1 : 3-diamines without difficulty.

2-Methylthioldihydropyrimid-6-one yields methyl mercaptan and trimethylenediamine when treated with sodium and alcohol, but it is not reduced by sodium amalgam. 2-Ethylthiol-5-ethoxydihydropyrimid-6-one is similarly reduced by sodium and alcohol with formation of trimethylenediamine. 2-Ethylthiol-4-methyldihydropyrimid-6-one yields $\alpha\gamma$-diaminobutane, $NH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot NH_2$; 2-ethylthiol-5-methyldihydropyrimid-6-one gives $\alpha\gamma$-diamino*iso*butane, $NH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot NH_2$, the *hydrochloride* of which has m. p. 196°; and 2-ethylthiol-1-methyldihydropyrimid-6-one furnishes α-amino-γ-methylaminopropane, $NHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot NH_2$, which yields a *hydrochloride*, m. p. 185—190°.

When 2-ethylthiol-4-methyldihydropyrimid-6-one, dissolved in an alcoholic solution of potassium hydroxide, is treated with methyl iodide, 2-*ethylthiol*-1 : 4-*dimethyldihydropyrimid*-6-*one*,

$$N\ll\begin{smallmatrix}C(SEt)\cdot NMe\\CMe{=\!=}CH\end{smallmatrix}>CO,$$

m. p. 63—64°, is produced, which crystallises in prisms, and is hydrolysed by hydrochloric acid with formation of ethyl mercaptan and 1 : 4-dimethyldihydropyrimid-6-one. On reduction with sodium and alcohol, 2-ethylthiol-1 : 4-dimethyldihydropyrimid-6-one yields γ-amino-α-methylaminobutane, $NHMe\cdot CH_2\cdot CH_2\cdot CHMe\cdot NH_2$, the *hydrochloride* of which has m. p. 223°.

When 2-thio-4-methyltetrahydropyrimid-6-one is reduced with sodium and alcohol, $\alpha\gamma$-diaminobutane is produced, which is converted by silver cyanate into the *dicarbamide*,

$$NH_2\cdot CO\cdot NH\cdot CH_2\cdot CHMe\cdot CH_2\cdot NH\cdot CO\cdot NH_2,$$

m. p. 172°, which crystallises in clusters of distorted needles. $\alpha\gamma$-Diaminobutane *picrate* has m. p. 240—245° (decomp.). E. G.

Pyrimidines. LXXIX. Synthesis of 4-Aldehydothymine. TREAT B. JOHNSON and LEONARD H. CRETCHER, Jun. (*J. Biol. Chem.*, 1916, **26**, 99—113).—The simple mononucleosides of uracil and thymine,

$$NH<\begin{matrix}CO-CH\\CO\cdot NH\end{matrix}>C\cdot CH_2\cdot OH \quad \text{and} \quad NH<\begin{matrix}CO\cdot CMe\\CO-NH\end{matrix}>C\cdot CH_2\cdot OH,$$

have been synthesised by a method which involved the condensation of thiocarbamide with ethyl γ-ethoxyacetoacetate and ethyl γ-ethoxy-α-methylacetoacetate respectively (A., 1913, i, 656; 1914, i, 1091). In order to obtain secondary alcohols of this series, thiocarbamide has been condensed with other β-ketonic esters of the type $OR\cdot CHMe\cdot CO\cdot CH_2\cdot CO_2Et$, where R = Me, Et, etc., and the syntheses have proved to be successful up to the point of isolating the ethers, $NH<\begin{matrix}CO-CH\\CO\cdot NH\end{matrix}>C\cdot CHMe\cdot OR$. All attempts to hydrolyse these, however, have led to abnormal compounds of apparently a new cyclic structure. It is hoped that the secondary alcohols will be synthesised by the action of Grignard agents on the corresponding aldehydes, and the preparation of uracil-4-aldehyde (A., 1915, i, 1002) is now augmented by the formation of the thymine derivative in anticipation of this.

Ethyl $\gamma\gamma$-diethoxy-α-methylacetoacetate (Dakin and Dudley, T., 1914, **104**, 2453) was prepared by the condensation of ethyl diethoxyacetate and ethyl propionate by the Claisen method. When heated with thiocarbamide and a solution of sodium ethoxide, it yielded 2-*thio*-5-*methyl*-4-*diethoxymethyltetrahydropyrimid*-6-*one*, $NH<\begin{matrix}CO\cdot CMe\\CS-NH\end{matrix}>C\cdot CH(OEt)_2$, which crystallised in large blocks, m. p. 119—120°, and this acetal was readily hydrolysed by hot hydrochloric acid to 2-*thio*-4-*aldehydothymine* (2-*thio*-4-*aldehydo*-5-*methyltetrahydropyrimid*-6-*one*). The aldehyde is colourless, but becomes yellow on heating; it has m. p. 232—233°, and reduces ammoniacal silver solutions, but not Fehling's solution. The *phenylhydrazone* forms long, prismatic needles, m. p. 287°; the *oxime* crystallises in hexagonal plates, decomp. 233°; the *anil*, $C_{12}H_{11}ON_3S$, separates in yellow, hexagonal plates, decomp. 274°.

The above acetal was heated with ethyl bromide and sodium ethoxide solution, and so converted into 2-*ethylthiol*-5-*methyl*-4-*diethoxymethyldihydropyrimid*-6-*one*, long needles, m. p. 100°, and this acetal was found to be very readily hydrolysed by 50% acetic acid to 2-*ethylthiol*-4-*aldehydo*-5-*methyldihydropyrimid*-6-*one*, $NH<\begin{matrix}CO-CMe\\C(SEt):N\end{matrix}>C\cdot CHO$, which crystallises in long needles, m. p. 186°, and does not readily reduce ammoniacal silver solutions. The *phenylhydrazone* forms yellow needles, decomp. 238°, and the *oxime* crystallises in elongated prisms, decomp. 235°. The acetal suffered the additional loss of ethyl mercaptan on hydrolysis with

hydrochloric acid, and was transformed directly into 4-*aldehydo-5-methyltetrahydropyrimid*-2 : 6-*dione* (4-*aldehydothymine*),

$$NH<\begin{matrix}CO\cdot CMe\\CO-NH\end{matrix}>C\cdot CHO,$$

which crystallised with $1H_2O$ or 1EtOH in colourless, prismatic needles or plates, m. p. 212—213°. The *phenylhydrazone* forms rosettes of yellow needles, decomp. 272°; the *oxime* crystallises in elongated, four-sided plates, decomp. 257°; the *anil* separates in long, yellow needles, decomp. 272°. J. C. W.

"Benzoyldihydromethylketol-hydrazine" [6-Hydrazino-1-benzoyl-2-methyldihydroindole] a New Reagent for Galactose. J. von Braun (*Ber.*, 1916, **49**, 1266—1268).—The author has converted many of the complicated, aromatic amines which he has discovered in recent years into the hydrazines in order to find, if possible, specific reagents for individual sugars. If 6-amino-1-benzoyl-2-methyldihydroindole (A., 1914, i, 436) is converted into the *hydrazine*, $NH_2\cdot NH\cdot C_6H_3<\begin{matrix}CH_2\\NBz\end{matrix}>CHMe$, colourless needles, m. p. 150—151°, a base is obtained which does not condense with dextrose, lævulose, mannose, arabinose, or xylose, but forms a *compound*, $C_{22}H_{27}O_6N_3$, with galactose, which separates as a colourless, crystalline mass, m. p. 181° (decomp.). The base also yields a *hydrochloride*, m. p. 197°, a *benzylidene* compound, m. p. 190—191°, a *semicarbazide*, m. p. 213°, and a *phenylthiosemicarbazide*, m. p. 204°. J. C. W.

The Valency of Two Directly Linked Nitrogen Atoms. I. Bawa Kartar Singh (T., 1916, **109**, 780—791).—An investigation for the purpose of producing further evidence in support of the view that, owing to steric interference, it is not possible for two directly linked nitrogen atoms to become quinquevalent at the same time (Singh, T., 1913, **103**, 604).

As a result of theoretical considerations the author arrives at a series of conclusions, for some of which he produces experimental confirmation.

Two quinquevalent nitrogen atoms cannot, on account of steric influence, be linked by their negative valencies. In agreement with this statement, it is not possible to cause methyl iodide or other alkyl haloids to react with an *as.*-phenylalkylhydrazine hydrochloride with production of the quaternary azonium iodide, although the latter is readily formed from the free base; nor is it possible to produce a salt of the type $NR_3X\cdot NH_3X'$ from azonium compounds of the structure $NR_3X\cdot NH_2$. In like manner, attempts to convert the azonium haloids into compounds containing two quinquevalent nitrogen atoms by the reaction $2NR_3X\cdot NH_2+2M=2MX+NH_2\cdot NR_3\cdot NR_3\cdot NH_2$, where X represents a halogen atom and M represents "molecular" silver or magnesium or zinc, were fruitless, the first metal failing to react, whilst the last two effected

the formation of ammonia and a tertiary amine. It is not possible to link two quinquevalent nitrogen atoms by their positive valencies probably for reasons of an electrical nature; compounds of the structure $NR_4 \cdot NR'_4$ would contain a nitrogen attached to five positive groups, an arrangement which does not seem capable of existence; nevertheless, it may be possible in the future to isolate compounds of the type $NR_4 \cdot NR'_3Cl$ in which one quinquevalent atom is linked by means of its positive valency to a second quinquevalent atom through a negative valency of the latter, because the spatial disposition of the bonds may not produce steric hindrance in this case.

From the above considerations it will not be possible to produce experimentally the nitrogen analogues of the tartaric acids, the nearest possible approach being compounds in which the two asymmetric nitrogen atoms are joined by a chain of carbon atoms such as the compounds of this type already described (Aschan, A., 1904, i, 350; Wedekind and Ney, A., 1913, i, 893).

It is possible that the above hypothetical considerations and deductions may be extended to other members of the nitrogen group of elements.

Benzylpropylaniline (*picrate*, yellow prisms, m. p. 145—146°), was obtained in the reaction of magnesium or zinc with a methyl-alcoholic solution of phenylbenzylpropylazonium iodide.

D. F. T.

Thermal Decomposition of Symmetrical Diarylhydrazines. JULIUS STIEGLITZ and HELEN TREDWAY GRAHAM (*J. Amer. Chem. Soc.*, 1916, **38**, 1736—1760).—Stieglitz and Curme (A., 1913, ii, 398) and Curme (A., 1913, ii, 854) investigated the velocity of the thermal decomposition of hydrazobenzene, $2NHPh \cdot NHPh \longrightarrow 2NH_2Ph + NPh\colon NPh$, and drew the conclusion that the reaction was one of the first order and that the hydrazobenzene underwent intermediate dissociation, thus: $NHPh \cdot NHPh \longrightarrow PhN\colon + NH_2Ph$. Wieland (A., 1912, i, 247) suggested, on the other hand, that the reaction consisted in the slow decomposition of the hydrazobenzene into azobenzene and atomic hydrogen, followed by the immeasurably rapid reduction of another molecule of hydrazobenzene by the hydrogen. This explanation, however, does not accord with the facts (1) that hydrogen does not seem to reduce hydrazobenzene under the conditions of the experiment, and (2) that no indication of the presence of free hydrogen was observed in any of Curme's experiments. These facts have both been confirmed in the present investigation.

If the reaction takes place in the manner suggested by Stieglitz and Curme, it would follow that in the decomposition of hydrazines with two different aryl groups, such as methylhydrazobenzene, $NHPh \cdot NH \cdot C_6H_4Me$, the preliminary dissociation into phenylimide radicles and anilines should yield ultimately three azo-compounds, $NPh\colon NPh$, $NPh\colon N \cdot C_6H_4Me$, and $C_6H_4Me \cdot N\colon N \cdot C_6H_4Me$, and two anilines, $C_6H_4Me \cdot NH_2$ and NH_2Ph. It has been found, however, that in the thermal decomposition of *p*-methylhydrazobenzene and

p-bromohydrazobenzene only one azo-compound is produced in each case, namely, NPh:N·C_6H_4Me and NPh:N·C_6H_4Br respectively. These results being irreconcilable with the theory of a preliminary dissociation into phenylimide radicles, the whole problem of the mechanism of the reaction was reopened.

The following facts were next established. For concentrations of 0·2—0·05 molar the reaction is one of the first order. In very dilute solutions (0·01—0·005 molar) the reaction is no longer clearly one of the first order, but is probably neither wholly of the first nor of the second order. When an alcoholic solution of bromohydrazobenzene is heated for two hours at 145° in an atmosphere of hydrogen, no absorption of hydrogen can be observed, and there is therefore no direct reduction with immeasurable speed. In extremely dilute solutions a little gas is produced, but hydrogen is absent. It is evident, therefore, that ordinary hydrogen cannot be an intermediate product in the thermal decomposition. The molecular weight of *p*-bromohydrazobenzene was determined in boiling alcohol and found to be that of the simple molecule, NHPh:NH·C_6H_4Br, and the explanation of a reaction of the first order between two molecules of hydrazobenzene as being due to a dimolecular form is thus excluded.

In order to reconcile the facts (1) that the thermal decomposition of hydrazines in solutions of moderate concentration (0·05—0·2 molar) is one of the first order, (2) that no ordinary decomposition product of the single molecule, namely, phenylimide, PhN:, or hydrogen, H_2, can be formed as an intermediate product, and (3) that a second molecule of the hydrazobenzene is nevertheless reduced with great rapidity as a result of the decomposition of the first molecule, the authors have proposed an explanation based on the electron theory of valence. According to this theory, when hydrazobenzene forms azobenzene and aniline, two electrons are discharged from the nitrogen of one molecule, producing azobenzene, and consequently releasing two positively charged hydrogen atoms; the nitrogen of the second molecule absorbs two electrons to form aniline, and this absorption causes the disruption of the union of the nitrogen atoms in this second molecule and gives the two negative radicles, NHPh·, the power to absorb two positively charged hydrogen atoms. The first slow decomposition reaction would thus be followed by an exceedingly rapid reduction reaction.

The velocity of decomposition of *p*-bromohydrazobenzene and of 2:4-dichlorohydrazobenzene at various concentrations has been determined, and the results are tabulated.

The conclusions drawn from the experiments described in this paper have been reached independently by Wieland (A., 1915, i, 850).

p-Bromohydrazobenzene has m. p. 101—101·5°. 2:4-*Dichloroazobenzene*, $C_6H_3Cl_2$·N:NPh, m. p. 105°, obtained by the action of nitrosobenzene on a solution of 2:4-dichloroaniline in glacial acetic acid, has a brilliant orange colour; it is accompanied by a *substance*, m. p. 139°, which forms pale green needles. On reducing 2:4-dichloroazobenzene in ammoniacal alcoholic solution with zinc

dust, 2:4-*dichlorohydrazobenzene*, $C_6H_3Cl_2\cdot NH\cdot NHPh$, m. p. 74·5°, is obtained, which crystallises in colourless plates. E. G.

Stereochemistry of Hydrazones of Esters of Dithiocarbonic Acids. II. M. BUSCH and FERD. BIEHLER (*J. pr. Chem.*, 1916, [ii], **93**, 339—362. Compare this vol., i, 338).—The simple semicarbazones and monophenylsemicarbazones of "mixed" esters of dithiocarbonic acid resemble the corresponding diphenylsemicarbazone derivatives (*loc. cit.*) in the capacity to exist in two stereoisomeric forms, but whereas the diaryl compounds under the influence of alkali readily undergo scission of mercaptan with concurrent condensation to triazolone derivatives, the simpler semicarbazones are remarkably resistant, recalling in this the behaviour of the hydrazones themselves. An endeavour to prepare stereoisomeric thiosemicarbazones of a similar type was not successful on account of the extreme instability of the desired substances; however, the nature of the decomposition products appeared to supply convincing evidence of stereoisomerism in the unisolated parent compounds.

Methyl semicarbazidodithiocarbonate, $NH_2\cdot CO\cdot NH\cdot NH\cdot CS_2Me$, was obtained by the successive addition of aqueous potassium carbonate solution, alcoholic potassium hydroxide, and carbon disulphide to an aqueous-alcoholic solution of semicarbazide hydrochloride, and treating the resulting solution of the *potassium* salt (an unstable solid crystallising in needles) with methyl iodide in the cold; the resulting ester, colourless needles, m. p. 191—192° (decomp.), has a distinctly acidic tendency and is easily soluble in dilute ammonia solution.

Benzyl semicarbazidodithiocarbonate,

$$NH_2\cdot CO\cdot NH\cdot NH\cdot CS_2\cdot CH_2Ph,$$

prepared in a similar manner to the methyl analogue, but with the use of benzyl chloride, forms colourless needles, m. p. 152—153° (decomp.). p-*Nitrobenzyl semicarbazidodithiocarbonate*,

$$NH_2\cdot CO\cdot NH\cdot NH\cdot CS_2\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

pale yellow needles, m. p. 176—177° (decomp.), was obtained in a similar manner, but care was necessary that the *p*-nitrobenzyl chloride should be added gradually and without excess, on account of the ease with which a second *p*-nitrobenzyl radicle enters the compound, with formation of *di*-p-*nitrobenzyl dithiocarbonate semicarbazone*, $NH_2\cdot CO\cdot NH\cdot N:C(S\cdot CH_2\cdot C_6H_4\cdot NO_2)_2$, brownish-yellow prisms, m. p. 150—151°.

By treating the above semicarbazidodithiocarbonates with an equivalent quantity of potassium hydroxide in alcoholic solution, the esters were converted into salts derived from the tautomeric structure $NH_2\cdot CO\cdot NH\cdot N:C(SR)\cdot SK$, from which the corresponding "mixed" esters could be prepared by treatment with an equivalent amount of alkyl haloid. In this way were produced *benzyl* syn.-*methyl dithiocarbonate semicarbazone*,

$$\begin{array}{l} NH_2\cdot CO\cdot NH\cdot N \\ \qquad\qquad\quad \| \\ \qquad\qquad SMe\cdot C\cdot S\cdot CH_2Ph \end{array}$$

colourless needles, m. p. 98° (*hydrochloride*, stout needles, m. p. 121—122° with decomp.; *potassium* derivative, leaflets), and its syn.-*benzyl methyl stereoisomeride*, $\begin{array}{r}NH_2\cdot CO\cdot NH\cdot N\\ \|\\ CH_2Ph\cdot S\cdot C\cdot SMe\end{array}$, colourless crystals, m. p. 82—83°, from the methyl and benzyl esters respectively of semicarbazidodithiocarbonic acid. Both stereoisomerides possess subdued basic and acidic properties and are of comparable solubility, but it was not found possible to convert either of the compounds into the other.

In an analogous manner the methyl and *p*-nitrobenzyl esters of semicarbazidodithiocarbonic acid were respectively converted into p-*nitrobenzyl* syn.-*methyl dithiocarbonate semicarbazone*,

$$\begin{array}{l}NH_2\cdot CO\cdot NH\cdot N\\ \qquad\qquad\qquad\quad\|\\ \qquad\qquad\quad SMe\cdot C\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2\end{array},$$

yellow prisms or needles, m. p. 168°, and the syn.-p-*nitrobenzyl methyl stereoisomeride*, $\begin{array}{r}NH_2\cdot CO\cdot NH\cdot N\\ \|\\ NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot C\cdot SMe\end{array}$, yellow needles, m. p. 152°. Again no success was attained in attempts to induce isomerisation in either of these compounds. Under the influence of mineral acids the isomerides underwent hydrolysis, giving ammonia, carbon dioxide, hydrazine, and p-*nitrobenzyl methyl dithiocarbonate*, $SMe\cdot CO\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2$, almost colourless needles or prisms, m. p. 69—70°; the substance, m. p. 168°, is very sensitive to alkalis, and is rapidly converted even by a cold dilute alcoholic alkaline solution into a yellow, amorphous product, whilst the isomeride, m. p. 152°, is unaffected under the same conditions.

Methyl phenylsemicarbazidodithiocarbonate,

$$NHPh\cdot CO\cdot NH\cdot NH\cdot CS_2Me,$$

was obtained by the interaction of methyl dithiocarbazinate and phenylcarbimide in benzene solution at low temperatures; it forms colourless needles, m. p. 190° (decomp.). *Benzyl phenylsemicarbazidodithiocarbonate*, $NHPh\cdot CO\cdot NH\cdot NH\cdot CS_2\cdot CH_2Ph$, silky needles, m. p. 184° (decomp.), was prepared in an analogous manner from benzyl dithiocarbazinate and phenylcarbimide. The former of these products reacted with benzyl chloride in the usual manner, giving *benzyl* syn.-*methyl dithiocarbonate semicarbazone*, $\begin{array}{r}NHPh\cdot CO\cdot NH\cdot N\\ \|\\ SMe\cdot C\cdot S\cdot CH_2Ph\end{array}$, colourless needles, m. p. 146—147°, whilst the latter with methyl iodide yielded the syn.-*benzyl methyl stereoisomeride*, $\begin{array}{r}NHPh\cdot CO\cdot NH\cdot N\\ \|\\ CH_2Ph\cdot S\cdot C\end{array}$, colourless needles or prisms, m. p. 156—157°. These stereoisomerides were feebly acidic substances. When fused, an equilibrium mixture was apparently produced, a small quantity of the *syn.*-methyl compound being obtained by recrystallisation of the melt from the isomeride of higher m. p.

In an endeavour to prepare methyl thiosemicarbazidodithiocarbonate, methyl dithiocarbazinate was converted into its *dihydrochloride*, colourless prisms, m. p. 165—166° (decomp.), and in this form allowed to react with a solution of excess of potassium thio-

cyanate. The product, however, was *2-thiol-5-methylthiol-1 : 3 : 4-thiodiazole*, $\begin{matrix} N\dot{:}C(SMe) \\ | \\ N{=}C(SH) \end{matrix}\!\!>\!S$, needles or leaflets, m. p. 136°, which was doubtless formed by the immediate intramolecular condensation of the ester primarily produced (compare Busch and Wolpert, A., 1901, i, 233). After the ordinary manner of a mercaptan, this compound was convertible by iodine into the corresponding *disulphide*, $C_6H_6N_4S_6$, yellow prisms, m. p. 77—78°; it also reacted in alkaline alcoholic solution with methyl iodide, yielding the corresponding *dimethyl* derivative as a fairly mobile oil, and with 1 : 3 : 4-*thiodiazole*, $\begin{matrix} N\text{———}N \\ \| \\ C(SMe)\cdot S \end{matrix}\!\!>\!C\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2$, pale yellow leaflets or needles, m. p. 115—116°. The compound described by Ziegele (A., 1899, i, 825) as 2 : 5-dimethyldithiol-1 : 3 : 4-thiodiazole is in reality the monomethyl compound.

Another attempt to prepare methyl thiosemicarbazidodithiocarbonate was made, starting with thiosemicarbazide itself. The reaction of this substance with carbon disulphide, potassium hydroxide, and methyl iodide in dilute alcoholic solution gave rise to a dimethyl *derivative*, $NH_2\cdot C(SMe)\dot{:}N\cdot NH\cdot CS_2Me$, colourless prisms, m. p. 101—102°, of thiosemicarbazidothiocarbonic acid; this substance is unstable, and when heated in alcoholic or benzene solution readily undergoes conversion into *2-amino-5-methylthiol-1 : 3 : 4-thiodiazole*, $\begin{matrix} N\dot{:}C(SMe) \\ | \\ N\dot{:}C(NH_2) \end{matrix}\!\!>\!S$, colourless needles or prisms, m. p. 177—178°; this behaves like a typical aromatic amine, yielding with nitrous acid a diazonium salt, which couples with β-naphthol giving *β-naphthol-2-azo-5-methylthiol-1 : 3 : 4-thiodiazole*, $OH\cdot C_{10}H_6\cdot N_2\cdot C\!\!<\!\!\begin{matrix} N\cdot N \\ \quad\| \\ S-C(SMe) \end{matrix}$, brownish-red needles, m. p. 167°.

The dimethyl derivative of thiosemicarbazidodithiocarbonic acid can be still further methylated by treating with excess of methyl iodide in alkaline solution, the product being *dimethyl dithiocarbonate* S-*methylthiosemicarbazone*, $NH_2\cdot C(SMe)\dot{:}N\cdot N\dot{:}C(SMe)_2$, colourless prisms, m. p. 59—60° (*hydrochloride*); in a similar manner, the introduction of the *p*-nitrobenzyl radicle gives rise to *methyl* p-*nitrobenzyl dithiocarbonate* S-*methylthiosemicarbazone*, $NH_2\cdot C(SMe)\dot{:}N\cdot N\dot{:}C(SMe)\cdot S\cdot CH_2\cdot C_6H_4\cdot NO_2$, yellow leaflets, m. p. 95—96°; *hydrochloride* and *sulphate*, crystalline, the latter having m. p. 177° (decomp.).

Methyl dithiocarbazinate and phenylthiocarbimide interact in warm alcoholic solution, yielding *methyl phenylthiosemicarbazidodithiocarbonate*, $NHPh\cdot CS\cdot NH\cdot NH\cdot CS_2Me$, leafy crystals, m. p. 136—137° (decomp.). This substance readily decomposes when heated in alkaline or alcoholic solution or when maintained at 140° for a short time, giving rise to hydrogen sulphide and anilino-5-methylthiol-1 : 3 : 4-thiodiazole, $\begin{matrix} N{=}C(SMe) \\ | \\ N\dot{:}C(NHPh) \end{matrix}\!\!>\!S$ (compare Busch and Schmidt, A., 1913, i, 907). Quite similarly to the last com-

pound, *benzyl phenylthiosemicarbazidodithiocarbonate*,

$$NHPh\cdot CS\cdot NH\cdot NH\cdot CS\cdot CH_2Ph,$$

was obtainable from benzyl dithiocarbazinate and phenylthiocarbimide; this substance forms quadratic leaflets, and at the m. p., 132°, loses hydrogen sulphide with formation of 2-anilino-5-benzylthiol-1:3:4-thiodiazole, $\begin{matrix} N\!:\!C(NHPh)- \\ | \\ N\!:\!C(S\cdot CH_2Ph) \end{matrix}\!\!>\!S$ (compare Busch and Schmidt, *loc. cit.*). When treated in alcoholic solution with potassium carbonate and benzyl chloride, methyl phenylthiosemicarbazidodithiocarbonate forms methyl mercaptan and the above-mentioned 2-anilino-5-benzylthiol-1:3:4-thiodiazole, whereas benzyl phenylthiosemicarbazidodithiocarbonate and methyl iodide under similar conditions give rise to benzyl mercaptan and 2-anilino-5-methylthiol-1:3:4-thiodiazole. These results are explicable by the formation of benzyl *syn.*-methyl dithiocarbonate phenylthiosemicarbazone, $\begin{matrix} NHPh\cdot CS\cdot NH\cdot N \\ \| \\ SMe\cdot C\cdot S\cdot CH_2Ph \end{matrix}$, and its *syn.*-benzyl stereoisomeride, $\begin{matrix} NHPh\cdot CS\cdot NH\cdot N \\ \| \\ CH_2Ph\cdot S\cdot C\cdot SMe \end{matrix}$, respectively, as unstable intermediate products in the two alkylation processes. D. F. T.

Hydrazino-diacids. J. R. BAILEY and L. A. MIKESKA (*J. Amer. Chem. Soc.*, 1916, **38**, 1771—1784).—Hydrazinodiacetic acid was discovered by Curtius and Hussong (A., 1911, i, 401), and further investigated by Bailey and Read (A., 1914, i, 1056). The only other hydrazino-diacid hitherto recorded is hydrazinodimalonic acid (Prabhakar, *Diss.*, 1912), but it is shown that the proofs advanced for the constitution of this substance are not valid. In the present paper an account is given of attempts to prepare other hydrazino-diacids.

When hydrazinodiacetic acid (1 mol.), dissolved in $2N$-potassium hydroxide (2 mols.), is shaken with a little less than the calculated quantity of benzaldehyde and subsequently acidified with hydrochloric acid, *benzylidenehydrazinodiacetic acid*,

$$CHPh\!:\!N\cdot N(CH_2\cdot CO_2H)_2,$$

m. p. 123° (decomp.), is produced, which forms long, slender prisms. The *potassium* salt is simultaneously formed, and decomposes at 210—215°; the *sodium, lead, barium,* and *calcium* salts were prepared.

By the condensation of salicylaldehyde with dipotassium hydrazinodiacetate, *potassium* o-*hydroxybenzylidenehydrazinodiacetate* is produced, which crystallises with $\frac{1}{2}H_2O$ and decomposes at 212°.

When a solution of potassium chloroacetate is boiled with alanine, and the product esterified by means of methyl alcohol and hydrogen chloride, and the solution evaporated, a residue is obtained which, when dissolved in water and treated with sodium nitrite, yields a nitrosoamine. On reducing the nitrosoamine in alcoholic solution with sodium amalgam, boiling the solution to

hydrolyse the ester of nitrosoiminoacetic–propionic acid, shaking the product with benzaldehyde and acidifying, the *sodium* salt of *benzylidenehydrazinoacetic–propionic acid* is produced, which decomposes at 330°. Salicylaldehyde yields the *sodium* salt of the corresponding salicylidene compound, m. p. 222°. When the ethyl ester of nitrosoiminoacetic–propionic acid is boiled with dilute hydrochloric acid, the *hydrochloride* of *iminoacetic–propionic acid*, $CO_2H\cdot CH_2\cdot NH\cdot CHMe\cdot CO_2H,HCl$, m. p. 223° (decomp.), is obtained.

Benzylidenehydrazinoacetic–iso*butyric acid*,

$$CHPh\colon N\cdot N(CH_2\cdot CO_2H)\cdot CMe_2\cdot CO_2H,$$

m. p. 202° (decomp.), forms short, slender needles; its *potassium* salt decomposes at 209°. The *potassium* salt of *benzylidenehydrazinodipropionic acid*, m. p. 210° (decomp.), can be obtained either from hydrazinopropionic acid or from benzylidenehydrazinopropionic acid, or by the following method. An aqueous solution of bromopropionic acid is treated with hydrazine hydrate; potassium carbonate is added, and the solution boiled and afterwards shaken with benzaldehyde, and neutralised with hydrochloric acid. Benzylidenehydrazinopropionic acid is also produced in this reaction.

When potassium benzylidenehydrazinodipropionate is suspended in water, treated with a little dilute hydrochloric acid, the benzaldehyde removed by distillation, the solution evaporated to dryness, the residue left for twelve hours with a saturated alcoholic solution of hydrogen chloride, the alcohol evaporated, and the residue dissolved in water and treated with potassium cyanate, *ethyl semicarbazinodipropionate*, $NH_2\cdot CO\cdot NH\cdot N(CHMe\cdot CO_2Et)_2$. m. p. 159° (decomp.), is obtained, which forms beautiful crystals.

By the action of potassium cyanate on a solution of benzylidenehydrazinopropionic acid in glacial acetic acid, *benzylideneaminomethylhydantoic acid*, $CHPh\colon N\cdot N(CO\cdot NH_2)\cdot CHMe\cdot CO_2H$, m. p. 180°, is produced, which forms diamond-shaped crystals, and is converted by dilute sulphuric acid into benzaldehyde and a crystalline compound, probably 1-amino-5-methylhydantoin. E. G.

Preparation of Acylsemicarbazides from Semicarbazones of α-Ketonic Acids. J. BOUGAULT (*Compt. rend.*, 1916, **163**, 237—239).—The semicarbazones of certain α-ketonic acids, when oxidised by iodine in the presence of sodium carbonate, give semicarbazides of acids containing one carbon atom less than the ketonic acid. The action takes place in the cold, the semicarbazone being dissolved in a little water containing an excess of sodium carbonate, and a solution of iodine in potassium iodide added. The acylsemicarbazide is precipitated at once. Thus the semicarbazone of phenylpyruvic acid gives *phenylacetylsemicarbazide*, $CH_2Ph\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$, m. p. 156°; benzylpyruvic acid semicarbazone gives *phenylpropionylsemicarbazide*, m. p. 192°; phenylglyoxylic acid semicarbazone yields benzoylsemicarbazide, m. p. 240°; and trimethylpyruvic acid semicarbazone yields *trimethylacetylsemicarbazide*, m. p. 215°. The semicarbazone of

pyruvic acid under similar conditions gives iodoform. The semicarbazides are alkaline in character and give crystalline hydrochlorides. If the oxidation is carried out in a solution so dilute that the semicarbazide remains dissolved, the action does not stop at this point, but the ultimate product of the oxidation is the free acid, nitrogen being liberated. This second phase of the reaction is much slower than the first. W. G.

Acylsemicarbazides. J. BOUGAULT (*Compt. rend.*, 1916, **163**, 305—307. Compare preceding abstract).—An account of the general properties of acylsemicarbazides. They have high melting points. They are very sparingly soluble in cold water and slightly more soluble in hot water. They are insoluble in benzene, chloroform, and light petroleum, alcohol being the most convenient solvent for their purification. They yield crystalline, stable hydrochlorides of the type $COPh \cdot NH \cdot NH \cdot CO \cdot NH_2,HCl$, which are dissociated by water and can be titrated with dilute sodium hydroxide, using phenolphthalein as an indicator. They are readily hydrolysed by boiling dilute acids or alkalis giving the acid and semicarbazide or its products of decomposition. Oxidising agents which attack and destroy the hydrazine group produce almost instantaneous hydrolysis of the acylsemicarbazides. This is particularly the case with alkali hypobromites or hypoiodites. With acetic anhydride they do not yield an acetyl derivative, but undergo hydrolysis. W. G.

Influence of Ethyl Alcohol and Glycerol on the Rate of Solution of Casein by Sodium Hydroxide. T. BRAILSFORD ROBERTSON and K. MIYAKE (*J. Biol. Chem.*, 1916, **26**, 129—142. Compare A., 1910, i, 528; this vol., i, 681).—In the earlier communications it was shown that the rate of solution of casein in an alkaline solvent depends on the velocity with which the particles are penetrated and wetted by the solvent, and that the amount of casein dissolved (x) in a given time (t) can be expressed by the formula $x = kt^m$, where the product of the two constants, km, is called the "penetration coefficient." The addition of alcohol and glycerol to the alkali solution, by reducing the surface tension, should therefore reduce the rate of penetration, and consequently of solution. Experiments along the same lines have therefore been carried out on the influence of varying quantities of these substances on the solution of casein in $0.016N$-sodium hydroxide, and the results support the above views. In the case of alcohol, however, there is a region in which the relationship between the coefficient of penetration and the concentration of alcohol is indefinite. This is between 4 and 8 molecular proportions of alcohol, and it is inferred that the discrepancy is due to the polymerisation of the casein molecules in this region.
J. C. W.

Conjugated Sulphuric Acid of Funis Mucin (Mucoitin-sulphuric Acid). II. P. A. LEVENE and J. LÓPEZ-SUÁREZ (*J. Biol. Chem.*, 1916, **26**, 373—378. Compare this vol., i, 681).—The con-

jugated sulphuric acid is obtained from umbilical cords by extraction with dilute sodium hydroxide solution. It is isolated as the barium salt, but the analytical figures obtained from different specimens vary considerably, and differ from those required by the formula $C_{28}H_{42}O_{29}N_2S_2Ba_2$, owing probably to a partial decomposition of the substance occurring during the process of purification. On hydrolysis, glucosamine hydrochloride was obtained and satisfactorily identified. H. W. B.

The Weighting of Silk with Stannic Chloride. A Chemical Reaction. FR. FICHTER and EMILE MULLER (*Arch. Sci. phys. nat.*, 1916, [iv], **42**, 123—141).—The authors consider that the weighting of silk by steeping it in a solution of stannic chloride is due to a true chemical combination between the stannic chloride and the fibroin and its component amino-acids, followed by hydrolysis, during the washing process. Certain experimental results are given in support of this theory.

When silk is steeped in benzene solutions of stannic chloride of varying strengths at the ordinary temperature and washed in benzene, the percentage increase in the weight of the silk, and the percentage of stannic oxide in it as found by ashing the silk, are constant and independent of the concentration of the original stannic chloride solution. Similar experiments performed with stannic bromide and iodide in xylene solution show that the percentages of chloride, bromide, and iodide absorbed are in the proportion 11·64 : 1·49 : 0·70.

The principal amino-acids in the fibroin of silk are glycine, alanine, and tyrosine, and it is found that when alanine (1 part) and stannic chloride (2 parts) are heated with benzene (2 parts) in a sealed tube at 140—150°, a definite *compound* is obtained as a transparent, colourless, vitreous mass having the composition $(CO_2H\cdot CHMe\cdot NH_2)_4,SnCl_4$. A similar *compound*,

$$(C_9H_{11}O_3N)_4,SnCl_4,$$

is obtained with tyrosine. Alanine with stannic bromide gives the *compound*, $(CO_2H\cdot CHMe\cdot NH_2)_4,SnBr_4$, under similar conditions, but the action does not go so easily. These compounds are only obtained at high temperatures, and similarly fibroin shows an increase of 9·7% in one hour at the ordinary temperature without any change in appearance, but at 140° it vitrifies and shows an increase of 34·5%. This reaction is not given by glycine or serine. The condensation compounds obtained are hygroscopic, and very soluble in water and alcohol. When dissolved in water and the solution slightly warmed, they undergo hydrolysis, and give a precipitate of gelatinous stannic acid. By partial hydrolysis in alcohol (96%) from the alanine compound there has been isolated a basic *compound*, $(CO_2H\cdot CHMe\cdot NH_2)_3,SnCl_3\cdot OH$. From glycine, by warming it with a solution of stannic chloride in its own weight of water and then adding alcohol, the basic *compound*,

$$(CO_2H\cdot CH_2\cdot NH_2),SnCl(OH)_3,$$

has been obtained. In the industrial process for the weighting of silk the maximum of absorption of stannic chloride by the

fibroin is by no means reached; after the hydrolysis during the washing process, the stannic acid is precipitated in the silk and the fibroin is regenerated with its original properties and is capable of taking up more stannic chloride.

In the latter part of the paper the authors discuss the action of phosphates in solution on gelatinous stannic acid, and show that the adsorption of sodium phosphate by the colloidal stannic acid does not change the ratio between acid and base. Further, the action is not chemical, but one of adsorption, the amount of sodium phosphate fixed varying with the strength of the solution.

W. G.

Dialysis of Trypsin and the Proteoclastic Action of the Protein Cleavage Products. CASIMIR FUNK (*J. Biol. Chem.*, 1916, **26**, 121—128).—Herzfeld (A., 1915, i, 469, 1019) has stated that the products of the action of trypsin on protein themselves possess proteoclastic power. The author finds, on the contrary, that trypsin, when subjected to dialysis in collodion bags, loses a large part of its amino-nitrogen, corresponding with the passage of amino-acids into the dialysate; but the dialysate does not possess proteoclastic properties, whilst the residue still retains, though to a less degree, the power of hydrolysing proteins. Various amino-acids and peptides have been tested for proteoclastic properties, but in all cases with negative results. The author's results do not therefore support Herzfeld's view that the action of trypsin is mainly due to the presence of amino-acids.

H. W. B.

Products of the Action of Certain Amylases on Soluble Starch, with Special Reference to the Formation of Dextrose. H. C. SHERMAN and P. W. PUNNETT (*J. Amer. Chem. Soc.*, 1916, **38**, 1877—1885).—The evidence with regard to the formation of dextrose by the action of amylase is very conflicting, and the question has therefore been reinvestigated.

In the experiments described, pancreatic and malt amylases and the amylase of *Aspergillus oryzae* were allowed to act on soluble starch under comparable and carefully controlled conditions, and the digestion products were examined both qualitatively and quantitatively for dextrose. The results show that any of these amylases may produce some dextrose, but that, under the conditions usually obtaining in determinations of diastatic power, the yield of maltose predominates to such an extent as to justify the custom of calculating the reducing powers of the digestion products as if they were due to maltose alone.

E. G.

Experiments on Starch as Substrate for Enzyme Action. H. C. SHERMAN and J. C. BAKER (*J. Amer. Chem. Soc.*, 1916, **38**, 1885—1904).—This investigation was undertaken with the object of preparing a substrate sufficiently homogeneous to yield trustworthy results in determinations of amyloclastic action by Wohlgemuth's method. A study has also been made of the different

behaviour towards enzymes of the two chief constituents of starch, namely, β-amylose, the more soluble constituent, and α-amylose, the less soluble.

By submitting thin starch paste containing a small quantity of sodium chloride to centrifugal force, it was separated into a heavier, viscous layer, containing α-amylose, and a lighter, limpid solution, containing β-amylose.

Comparative experiments were made on the action of enzymes on α-amylose, β-amylose, autoclaved starch, and Lintner soluble starch. Pancreatic amylase produced reducing sugar from β-amylose more rapidly than from any of the other three substrates, and the initial speed of hydrolysis was better maintained. Purified malt amylase, in the earlier stages of its action, gave a larger yield of maltose from α- than from β-amylose, but as a final result the β-amylose showed the greater saccharogenic hydrolysis; autoclaved starch and Lintner soluble starch behaved similarly to the α-amylose. The amylase of *Aspergillus oryzae* digests Lintner soluble starch, autoclaved starch, and α-amylose at about equal rates, and β-amylose at a somewhat greater rate, but its action on β-amylose is not so well sustained as that of pancreatic or malt amylase.

The three amylases catalyse the successive stages of the hydrolysis of β-amylose and its products at relatively different velocities. The time curve for pancreatic amylase is practically logarithmic until about three-fourths of the theoretical amount of maltose has been produced, but the action then proceeds more slowly. In comparison with this result, the catalytic effect of the amylase of *Aspergillus oryzae* is more pronounced in the earlier and less pronounced in the later stages, whilst the reverse is true of the malt amylase. In the digestion of α-amylose, all the amylases showed greater catalytic effect on the earlier than on the later stages of the digestion. Starch pastes made at 65—80°, autoclaved starch, and Lintner soluble starch all resemble the α-amylose rather than the β-amylose substrate in their behaviour towards each of the three amylases.

The results of these experiments show that Lintner soluble starch is well adapted to its purpose as substrate for testing the activities of the different amylases, and that its use leads to conservative estimates of the diastatic powers of purified preparations.

When tested on any of the four substrates used in this work, the three amylases show distinctly different ratios of amyloclastic to saccharogenic powers. E. G.

Amylase of Aspergillus Oryzae [Taka-diastase]. H. C. SHERMAN and A. P. TANBERG (*J. Amer. Chem. Soc.*, 1916, **38**, 1638—1645).—Taka-diastase exerts its maximum activity in a very slightly acid medium; sodium dihydrogen phosphate accelerates, whilst the alkaline trisodium phosphate retards the action. Neutral electrolytes, such as sodium and potassium chlorides, slightly increase the rate of action of the commercial taka-diastase.

A comparatively pure form of taka-diastase can be prepared from the commercial article by extracting with water, precipitating with ammonium sulphate, dissolving the precipitate in water, dialysing,

and finally precipitating fractionally with alcohol. Such a preparation has about thirty times the activity of the commercial article from which it is prepared, but it is not so active as purified pancreatic diastase, although, otherwise, in its chemical properties it closely resembles it. It gives the typical protein reactions, and coagulates when heated in aqueous solution. It contains less nitrogen than pancreatic diastase, but this may be due to the presence of non-nitrogenous material not removed by the process of purification adopted. H. W. B.

Physiological Chemistry.

The Respiratory Metabolism of Normal and Anæmic Subjects Performing Light Muscular Work. SHIGESHI KAKEHI (*Biochem. Zeitsch.*, 1916, **76**, 248—274).—The experiments were carried out on men and women in a Jacquet respiration chamber. The mean of the experiments on normal subjects at rest showed a production of carbon dioxide of 3·43 c.c. per kilo. of body weight per minute, and an oxygen consumption of 3·90 (respiratory quotient, 0·877). For anæmic subjects, the corresponding numbers were 3·69 and 4·19 c.c. ($R\,.\,Q=0{\cdot}882$). The two sets of figures do not differ very largely, especially as regards the respiratory quotients. There is, however, a distinct, although not very marked, difference in the respiratory quotients of normal and anæmic individuals when the subjects are performing muscular work. The increased oxygen consumption of anæmic subjects is, under these conditions, larger than that of normal persons. The author remarks, however, that he has not investigated a sufficient number of cases for any decisive statement on this point. S. B. S.

The Blood of Participators in an Army March with Accoutrements. I. The Changes and Excretion of Blood Pigment. Hæmoglobinæmia, Hæmatinæmia, and Hæmoglobinuria. JOH. FEIGL, with A. V. KNACK and H. KOOPMANN (*Biochem. Zeitsch.*, 1916, **76**, 88—106).—The blood-sera were examined spectroscopically by Schumm's spectroscope, both before and after the march. As a result of over-exertion, both hæmoglobinæmia and hæmatinæmia were observed, in some cases together, in other cases separately. Of the cases in which the sera contained hæmatin or hæmoglobin, about 66% exhibited urines containing dissolved blood pigment without erythrocytes. In those cases where the sera contained both hæmatin and hæmoglobin, about 80% exhibited dissolved blood pigment in the urine, and the remainder both pigment and erythrocytes. Finally, in more than 70% of the cases when the sera were normal and the urine gave positive blood reactions, erythrocytes could be detected by microscopic examination.

S. B. S.

Enzymic Actions of Blood on Dextrose. IV. Enzymic Properties of the Blood of the Depancreatised Dog, before and after Circulation (with Dextrose) in the Intestine of the same Animal. UGO LOMBROSO (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 83—87. Compare this vol., i, 612, 686).—The blood of the depancreatised dog exhibits a synthesising action towards dextrose almost equal to that of normal blood, but the glycolytic power is more or less profoundly diminished, although not destroyed completely; the greatest observed diminution of the glycolytic power does not correspond with the greatest lapse of time since depancreatisation. The consumption of dextrose dissolved in diabetic blood by the intestine of the same animal is markedly less than that occurring with a normal intestine in the same period of time; the least consumption of dextrose was observed with the intestine of the dog depancreatised for the longest time. The blood of the depancreatised dog, when circulated in the intestine of the same animal, exhibits the presence of a highly active glycolytic enzyme capable of destroying, during the first few hours in the thermostat, 10—50% of the dextrose remaining in the blood after circulation (compare Edelmann, A., 1912, ii, 572; Macleod and Pearce, A., 1913, i, 937; Macleod and Wedd, A., 1913, i, 1258). T. H. P.

Enzymic Actions of Blood on Dextrose. V. Glycolysis of Blood Circulated with Dextrose in the Liver, Spleen, Kidney, or Muscle. UGO LOMBROSO (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 115—120, Compare preceding abstract).—When blood containing dextrose is circulated through the spleen, kidneys, or muscle, the dextrose undergoes more or less marked diminution in amount. When, however, the circulation takes place through the liver, the blood is afterwards richer in dextrose. The condensation of dextrose in the blood as a result of circulation in the above organs does not exceed that observed in normal blood. T. H. P.

Assumed Destruction of Trypsin by Pepsin and Acid. J. H. LONG and MARY HULL (*J. Amer. Chem. Soc.*, 1916, **38**, 1620—1638. Compare Long and Johnson, A., 1913, i, 919, 1118). —The destruction of trypsin by pepsin and acid is retarded or prevented by the addition of protein, which causes a reduction in the concentration of hydrogen ion in the mixture. A tablet containing active trypsin may therefore escape destruction in the stomach, and on passing into the duodenum assist to a certain extent the normal digestion of proteins. H. W. B.

Chemical Nature of the Vitamines. II. Isomerism in Natural Antineuritic Substances. ROBERT R. WILLIAMS and ATHERTON SEIDELL (*J. Biol. Chem.*, 1916, **26**, 431—456. Compare this vol., i, 697).—A *substance*, m. p. 345°, possessing antineuritic properties has been isolated from autolysed yeast. On purification by repeated crystallisation from hot water, it loses its antineuritic power, and changes its crystalline form. On analysis, the inactive material is found to be adenine. When adenine is fused by heat

or heated with absolute alcohol in a sealed tube at 180° for three hours, the antineuritic power is restored. The active substance gives a blue coloration with Folin's phosphotungstic acid reagent and sodium carbonate, which is not given by the inactive substance. It is suggested that the active antineuritic substance is an isomeride of adenine. H. W. B.

Effect of the Amino-acid Content of the Diet on the Growth of Chickens. THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, EDNA L. FERRY and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1916, **26**, 293—300).—The feeding experiments of Buckner, Nollau, and Kastle (this vol., i, 102) on chickens have been repeated, using corn gluten containing about 1% of lysine as the chief source of protein with and without the addition of cotton-seed flour and of lactalbumin containing 10% of lysine. During the test period of fifty-five days, the chicken on the corn-gluten diet increased in weight by 52 grams, whilst the chickens receiving the additional lysine-rich proteins put on 322 and 283 grams respectively. The results are strikingly illustrated by photographs of the chickens, and confirm the statements previously made regarding the unequal value of different proteins in the nutrition of growth. H. W. B.

Relation of the Quality of Proteins to Milk Production. E. B. HART, G. C. HUMPHREY, and A. A. SCHAAL (*J. Biol. Chem.*, 1916, **26**, 457—471. Compare A., 1915, i, 742).—Using a basal ration consisting of corn stover, corn meal, silage, and starch, the authors have ascertained the efficiency for milk production of the common protein concentrates used in feeding milking animals. The total protein intake constituted about 10% of the dry matter of the food, and 50% of the total digestible protein was furnished by the added protein concentrate. The utilisation of the protein in the concentrates for milk production was calculated to be as follows: gluten feed, 45; oil meal, 61; distiller's grains, 60; casein, 59; and skim milk powder, 60. The quality of the protein in the food has therefore a distinct influence on the quality and quantity of the milk produced.

The three cows used in the experiments each produced 40 to 45 lb. of milk daily containing 10 to 12% of total solids. Throughout the experiments, which extended for sixteen weeks, the analyses showed a negative nitrogen balance. Only during the period of skim milk powder feeding was one of the animals storing nitrogen. In spite of this long negative balance, milk secretion continued at the expense of catabolising tissue, although a slight diminution in the total yield and total solids of the milk was observed after about eight weeks. The animals lost about 70 to 80 lb. in weight during the experiment, and at the close were distinctly emaciated and partly depleted of muscular tissue.

H. W. B.

Urea Formation in the Isolated Liver of Warm-blooded Animals. WILHELM LÖFFLER (*Biochem. Zeitsch.*, 1916, **76**, 55—75) —The perfusion with blood of the livers of dogs and rabbits which

have been removed from the animals after they have fasted for three days does not lead to an increase in urea. On the other hand, an appreciable amount of urea is formed during perfusion if the liver has been removed during the height of digestion. Addition of ammonium salts, or of glycine, alanine, leucine, aspartic acid, and serine, to the perfusing fluid causes considerable increase in the urea; no appreciable increase is produced, however, by tyrosine, cystine, or taurine. S. B. S.

Detection of Fermentation Enzymes in the Animal Body. BETH EULER and HANS EULER (*Zeitsch. physiol. Chem.*, 1916, **97**, 311—313).—When pyruvic acid is incubated with ox liver, an evolution of carbon dioxide occurs which is not observed when the kidneys or pancreas is substituted for the liver. The authors suggest that (1) the liver contains a carboxylase, or (2) bacteria peculiar to the liver decompose the pyruvic acid. H. W. B.

Creatine in Human Muscle. W. DENIS (*J. Biol. Chem.*, 1916, **26**, 379—386).—Human psoas muscle from normal adults contains from 360 to 421 mg. of creatine per 100 grams of muscle.

Under pathological conditions it is found that when emaciation occurs during the course of the disease, the amount of creatine in the muscle examined after death is considerably reduced. When emaciation does not take place, the creatine content of the muscle remains about normal.

The muscle from children contains much less creatine than that from adults. H. W. B.

Detection of Selenium in Bones and Teeth. TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1916, **97**, 307—310).—The ash from bones or teeth is dissolved in aqua regia and the selenium precipitated by hydrogen sulphide. The precipitate is dissolved in ammonia and a few drops of ammonium sulphide, and again precipitated by warm hydrochloric acid. It is then oxidised to selenic acid by the action of nitric acid, and can be identified by crystalline form, or by conversion into the brown selenious acid.

Selenium appears to be a constant constituent of teeth and bones. H. W. B.

The Formation of Glycine in the Animal Body. GEORG HAAS (*Biochem. Zeitsch.*, 1916, **76**, 76—87).—According to the views of Hofmeister as to the degradative oxidation of proteins in the animal body, aminomalonic acid is a possible intermediary product and a precursor of glycine. This acid was found to be very toxic to the organism, especially as regards the respiratory and vascular centres, and to be not readily combustible. No evidence could be discovered that it is a precursor of glycine, whether in experiments on the whole organism, or in the isolated liver, or with organ paste. No hippuric acid was found after administration of benzoylaminomalonic acid. In liver-perfusion experiments with glutamic and aspartic acids, with the sodium hydrogen

sulphite compound of glyoxal in presence of ammonium acetate, negative results as regards glycine formation were also obtained.

S. B. S.

Distribution of Urea in the Blood and Tissues of certain Vertebrates with Special Reference to the Hen. WALTER G. KARR and HOWARD B. LEWIS (*J. Amer. Chem. Soc.*, 1916, **38**, 1615—1620).—The authors have estimated the amount of urea in the blood and other tissues of the guinea-pig, rabbit, turtle, and hen by Marshall and Davis's method (A., 1914, i, 901). The kidney in the cases of the guinea-pig and rabbit contains more urea than any other tissue, whilst in the hen and turtle all the tissues contain about the same percentage amount of urea, which is considerably lower than that found in the corresponding tissue of the guinea-pig or rabbit.

When urea is injected into a hen, it is transferred to all tissues of the body. After the injection of alanine an increase in the urea content of the tissues does not occur, indicating that urea is not one of the intermediate stages in the metabolism of amino-acids in the hen.

H. W. B.

Relative Excretion of Phenols by the Kidneys and by the Intestine. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1916, **26**, 507—513).—The colorimetric method for the estimation of phenol in urine (Folin and Denis, A., 1915, ii, 802) has been applied to the estimation of phenol in fæces. From the results of an examination of the urinary and intestinal excretion of phenol in normal men, the authors draw the conclusion that, in the absence of diarrhœa, laxatives, and enemata, a small fraction (from 7 to 20%) of the phenols formed is eliminated by the intestine. The phenol in the fæces is entirely in the free, unconjugated form.

H. W. B.

Aromatic Constituents of Urine. I. Non-phenolic Volatile Oils of Cow's Urine. R. J. ANDERSON (*J. Biol. Chem.*, 1916, **26**, 387—400).—The oil obtained from cow's urine by distillation with sulphuric acid, which has been termed "Urogon" by Mooser (A., 1909, ii, 1039), is separated by fractional distillation in a vacuum into two fractions, one of which is found to be identical with *p*-cresol (Mooser's "Urogol"), whilst the other distils at 102°/1 mm. and has the empirical formula $C_{10}H_{16}O$. The latter *substance*, which is isomeric with camphor, reduces ammoniacal silver nitrate on heating, decolorises permanganate solution, and in chloroform solution absorbs bromine with liberation of hydrogen bromide. It does not react with phenylcarbimide, phenylhydrazine, or sodium hydrogen sulphite, but a *semicarbazone*, $C_{10}H_{16}$:N·NH·CO·NH_2, m. p. 165°, was obtained, in colourless plates, from dilute methyl alcohol.

The oil obtained from cow's urine in winter differs somewhat from that obtained in summer, probably owing to the different food consumed. Both contain a large proportion of *p*-cresol, but the

substance, $C_{10}H_{16}O$, could only be isolated in a pure condition from the summer urine. H. W. B.

Aromatic Constituents of Urine. II. Non-phenolic Volatile Oils of Goat's Urine. R. J. ANDERSON (*J. Biol. Chem.*, 1916, **26**, 401—408. Compare preceding abstract).—The oil contains principally *p*-cresol mixed with a small percentage of the non-phenolic volatile oil, $C_{10}H_{16}O$, previously isolated from cow's urine.
H. W. B.

Aromatic Constituents of Urine. III. Non-phenolic Volatile Oils of Horse's and Human Urine. R. J. ANDERSON (*J. Biol. Chem.*, 1916, **26**, 409—415. Compare preceding abstract).—A non-phenolic volatile oil has been isolated from the urine of the horse and of man which closely resembles in properties the corresponding substance previously obtained from the urine of the cow and of the goat. The elementary composition, however, agrees more nearly with the formula $C_7H_{12}O$ instead of $C_{10}H_{16}O$.

Of all the urines examined, that from human beings contains the smallest percentage of neutral oil. The "Urinod" of Dehn and Hartman (A., 1914, i, 1188) is shown to consist probably of a mixture of the above neutral oil and *p*-cresol. H. W. B.

Creatine and Creatinine. V. Protein Feeding and Creatine Elimination in Pancreatic Diabetes. WILLIAM C. ROSE (*J. Biol. Chem.*, 1916, **26**, 331—338. Compare Benedict and Österberg, A., 1914, i, 1025, and Wolf, A., 1912, ii, 270).—Since the inhibition of the excretion of creatine which occurs in a fasting dog on feeding with protein (Wolf, *loc. cit.*) may be due to the well-recognised inhibiting action of dextrose formed from the protein in the animal organism, the author has studied the effect of protein feeding on depancreatised dogs. In these circumstances, in which dextrose is incapable of preventing the elimination of creatine in the urine, protein feeding does not arrest the continued elimination of urinary creatine, which is in harmony with the results of Benedict and Österberg (*loc. cit.*) obtained in the phloridzinised animal. The author still maintains, therefore, that the excretion of creatine is due to a disturbance of carbohydrate metabolism.
H. W. B.

Creatine and Creatinine. VI. Protein Feeding and Creatine Elimination in Fasting Man. WILLIAM C. ROSE, FRANK W. DIMMITT, and PAUL N. CHEATHAM (*J. Biol. Chem.*, 1916, **26**, 339—344. Compare preceding abstract).—After starvation for three or four days, the administration of protein food (eggs) rapidly causes the disappearance of creatine from the urine. This was not observed by Cathcart (A., 1909, ii, 1032), owing probably to the short duration of his fasts. H. W. B.

Creatine and Creatinine. VII. Fate of Creatine and Creatinine when Administered to Man. WILLIAM C. ROSE and FRANK W. DIMMITT (*J. Biol. Chem.*, 1916, **26**, 345—353).—The

ingestion of 20 grams of creatine leads, in man, to a distinct increase in the output of urinary creatinine, although by far the larger portion of the creatine reappears as such in the urine. Ingested creatinine passes unchanged through the body; a conversion of creatinine into creatine does not occur. H. W. B.

Toxicity, Sensitising Power, and Spectroscopic Behaviour of the Natural Porphyrins. Degradation of Urinoporphyrin to Cotoporphyrin. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1916, **97**, 109—127. Compare this vol., i, 575).—Urinoporphyrin is converted into cotoporphyrin by boiling the methyl ester in acetic acid solution with phosphorus and hydriodic acid. After removal of unchanged urinoporphyrin by precipitation with sodium hydroxide, the cotoporphyrin which has been produced is extracted with ether and identified by conversion into the crystalline methyl ester and complex copper salt (*loc. cit.*). By means of this reaction four carboxyl radicles are removed from the urinoporphyrin molecule.

Experiments with white mice show that for these animals cotoporphyrin is twice as toxic as urinoporphyrin when the mice are kept in the dark. When exposed to sunlight the effects are reversed, and urinoporphyrin becomes almost as toxic as hæmatoporphyrin. A striking symptom is the development of a strong red colour in the skin of the hairless portions of the animal—in the tail, nose, and especially the cartilages of the ears.

Measurements of the absorption bands in the spectra of the naturally occurring porphyrins are appended. H. W. B.

Porphyrins in Pathological Urine and Fæces. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1916, **97**, 148—170. Compare this vol., i, 575).—Cotoporphyrin is present in small amounts in company with urinoporphyrin in pathological urine, and can be separated from the mixed esters by hydrolysis and subsequent extraction with ether, in which urinoporphyrin is almost insoluble. Neither porphyrin can be detected in the serum of the blood.

The *zinc* salt of *trimethylurinoporphyrin*, $C_{47}H_{48}O_{16}N_4Zn$, crystallises from a mixture of trimethylurinoporphyrin and zinc acetate in glacial acetic acid solution. Its alcoholic solution possesses an intense red fluorescence, and spectroscopic examination shows two absorption bands. The corresponding *zinc* salt of *trimethylcotoporphyrin*, $C_{39}H_{40}O_8N_4Zn$, has similar properties.

By treatment with sodium amalgam, both urinoporphyrin and cotoporphyrin are converted into leuco-compounds, which, however, have not been isolated. On shaking with air, the colouring matters are re-formed. H. W. B.

Hæmatin as a Pathological Constituent of Blood. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1916, **97**, 32—52. Compare A., 1913, ii, 892).—A large number of samples of pathological blood have been examined for the presence of hæmatin by the method previously described (*loc. cit.*). Positive results were obtained in cases where

an abnormal destruction of red blood corpuscles occurred, such as pernicious anæmia, malaria, eclampsia, acute toxic conditions occasioned by certain organic and inorganic poisons, etc. The hæmatin was sometimes accompanied by methæmoglobin or bilirubin. H. W. B.

New Type of Glycosuria. Glucosomethylpentosuria. As. ZLATAROFF (*Zeitsch. physiol. Chem.*, 1916, **97**, 28—31).—A case of severe diabetes mellitus is reported in which the urinary dextrose was apparently accompanied by rhamnose. The rhamnosazone was separated from glucosazone by extraction with warm water, and after recrystallisation from acetone gave, on elementary analyses, the required figures, and m. p. 187°. The osazone was decomposed by formaldehyde, and the free sugar, after crystallising from water, had m. p. 122° and $[\alpha]_D + 8{\cdot}50$. The amount of rhamnose in the urine was estimated to be about 2%.

H. W. B.

Lipoids ("Fat") of the Blood in Diabetes. W. R. BLOOR, E. P. JOSLIN and A. A. HORNOR (*J. Biol. Chem.*, 1916, **26**, 417—430).—In severe diabetes the quantity of lipoids in the blood is markedly increased, amounting to 100% or more of the normal value. In spite of the high values, the relations between the various lipoids are practically normal, indicating that fat metabolism is also essentially normal (compare Bloor, this vol., i, 450). The increase in the lipoids in diabetes is confined to the plasma, the composition of the corpuscles remaining as in health. Since the cholesterol in the plasma of diabetics runs parallel to the other lipoids, the estimation of cholesterol in plasma is sufficient to afford valuable information regarding the lipoid content of the blood in diabetes.

Lipæmia was only present in two out of the forty cases investigated. H. W. B.

Fate of Ingested Starch in Phloridzin Diabetes. FRANK A. CSONKA (*J. Biol. Chem.*, 1916, **26**, 327—329).—Starch given to phloridzinised dogs either in the form of wheat flour or of oatmeal is quantitatively eliminated as dextrose in the urine.

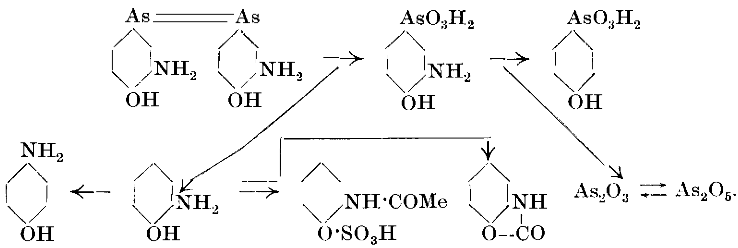
H. W. B.

Effects of Temperature and Fever on the Synthesis of Conjugated Sulphuric and Glycuronic Acids in the Organism. HIIZU ITO (*J. Biol. Chem.*, 1916, **26**, 301—318).—When abnormal temperatures are induced in rabbits by chilling in water, warming in hot air, or creating fever by pus injections, the amount of conjugated sulphuric or glycuronic acid formed after the administration of phenol or chloral hydrate is less than is formed under normal conditions. The more abnormal the condition, the more the conjugating function is prevented. H. W. B.

Accumulation of Uric Acid in the Tissues During Suppression of Urine. H. GIDEON WELLS (*J. Biol. Chem.*, 1916, **26**, 319—326).—In a case of anuria in which almost complete suppression of urine occurred for nine days, the following amounts of uric acid were isolated in a pure state after death from the tissues:

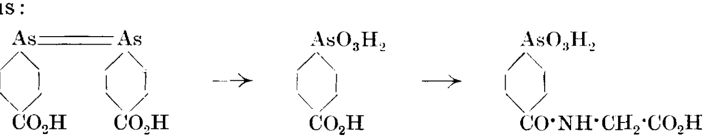
intestine, 6 mg.; blood, 2·5 mg.; liver, 1 mg. per 100 grams of moist tissue. Tissues from persons dying from various causes were found to be practically free from uric acid. Failure of the excretory function of the kidney leads, therefore, to accumulation of uric acid in the tissues. H. W. B.

Biology of Aromatic Arsenic Compounds. ERNST SIEBURG (*Zeitsch. physiol. Chem.*, 1916, **97**, 53—108).—After repeated intravenous injections of salvarsan into a syphilitic patient, the following substances are found in the urine: *p*-aminophenol, *o*-acetylaminophenyl hydrogen sulphate, oxycarbanil, on *amino-hydroxyphenylarsinic acid*, $C_6H_8O_4NAs$, and a *hydroxyphenylarsinic acid*, $C_6H_7O_4As$, besides inorganic arsenates and arsenites. The new phenylarsinic acids are obtained by extracting the urine with ethyl acetate, and subsequently treating the extract with water and concentrating to a small bulk in an atmosphere of carbon dioxide. The aminohydroxy-compound crystallises in needles, and on the addition of alcohol to the mother liquor, small, white needles of the hydroxyphenylarsinic acid are obtained. Salvarsan is therefore broken down in the system in the following way:



Apparently *o*-aminophenol is to a comparatively small extent converted into the isomeric, highly toxic para-compound, whilst the remainder is conjugated either with sulphuric acid with the introduction of an acetyl group, or with carbamide with subsequent elimination of two ammonia radicles (compare Sandmeyer, A., 1887, 135).

The behaviour of *p*-arsenobenzoic acid in the animal organism has been ascertained by repeated subcutaneous injections of the substance into a calf, and subsequent examination of the urine. The chief excretory product is p-*carboxyphenylarsinic acid*, $C_7H_7O_5As$, which is obtained, by extraction of the concentrated urine with alcohol, in the form of small, colourless needles which do not have any melting point. The *silver* salt, $C_7H_4O_5AsAg_3$, was also prepared. From the mother liquor, crystals of *hippuro-arsinic acid* were isolated, the amino-acid constituent of which was recognised by means of its β-naphthalenesulphonic derivative. The metabolism of *p*-arsenobenzoic acid can therefore be represented thus:



The injection of *p*-arsenobenzoic acid appears to derange normal metabolism, because during the treatment large quantities of benzoic and glycuronic acids are eliminated in the urine. Arsenic and arsenious oxides are also found in the urine.

In confirmation of the above results, it is found that the subcutaneous injection of 3-aminoarsenobenzoic acid is followed by the elimination of 3-*acetylamino*-p-*benzarsinic acid* (3-*acetylamino*-4-*carboxyphenylarsinic acid*), white needles, which decompose above 250° without melting. In all cases, therefore, a cleavage of the toxophoric ·As=As· linking in 'arseno' compounds occurs in the living organism, whereby not only is the toxicity reduced, but transformation takes place into compounds which are more soluble in water and less easily soluble in other media. The characteristic effects of salvarsan are due to the small proportion of the substance which escapes oxidation to the arsinic acids, and to the subsequent liberation of the arsenic and arsenious oxides.

H. W. B.

The Parenteral Injection of Sucrose, and the Supposed Formation of Invertin. G. O. FOLKMAR (*Biochem. Zeitsch.*, 1916, **76**, 1—54).—By subcutaneous, intravenous, or permanent intravenous injection (by the method of Henriques) of sucrose, a part of the sugar is retained in the organism in the case of most of the animals investigated (goats, dogs, rabbits) which in certain cases can amount to 60% of the amount injected. In other animals (sheep, pigs) the whole of the injected sugar appears in the urine. When very large amounts of sugar are injected, the kidneys appear to be injured, and this accounts for the large retention. No adaptation as regards capacity for retention of sugar parenterally administered can be brought about by the addition of large amounts of sugar to the daily diet. In no case did the blood of any animal to which the sucrose had been given parenterally contain invertin.

S. B. S.

The Pharmacological Action of Hypophysin. HERMANN FÜHNER (*Biochem. Zeitsch.*, 1916, **76**, 232—247).—In the preparation described by the author of hypophysin from pituitary extract there is no great loss of the substances of the glands which exert an effect on the blood-pressure and uterus. A comparison of the action of hypophysin with that of pilocarpine and the esters of choline shows very marked differences of action. One of the most striking is that the action of hypophysin is not antagonised by atropine, whereas quite small doses suffice to antagonise the action of the other substances. These reasons are sufficient to render improbable the assumption that has been made that the active substances of the pituitary body are esters of choline.

S. B. S.

General Conceptions of Intoxication. MARTIN JACOBY (*Biochem. Zeitsch.*, 1916, **76**, 275—296).—The urease ferment is rendered inactive by the minutest amounts of mercuric chloride,

to which, whatever the quantity, no accelerative action can be ascribed. The ferment inactivated by the mercury salt can be reactivated by potassium cyanide. A relatively large amount of this salt is necessary to diminish the activity of the urease, but medium quantities cause a distinct, but not very large increase in its activity. Nickel oxide (insoluble in water) inactivates an aqueous solution of the ferment; after separation from the nickel oxide it can be reactivated by potassium cyanide. Ferment rendered inactive by mercuric chloride cannot be reactivated by glycine, whereas if rendered inactive by nickel oxide it can be reactivated by small quantities of this substance. The scission of urea by bacteria is inhibited both by mercuric chloride and potassium cyanide, neither substance exerting a stimulating action in very small concentrations. Bacteria the ureaclastic activity of which has been destroyed by the mercury salt are not rendered reactive in this respect by potassium cyanide. The doses of nickel oxide, mercuric chloride, and potassium cyanide which stop the ureaclastic action do not kill the bacteria. Bacteria which act on urea do not act on methylurea, thiourea, or acetamide. The author distinguishes between two types of toxic action; substances exerting the one type of action kill the ferment, whereas those belonging to the other only inhibit the fermentative action. S. B. S.

[The Amount of] Morphine in the Various Organs after Injection into Cats and Rabbits. A. W. HOMBERGER and J. C. MUNCH (*J. Amer. Chem. Soc.*, 1916, **38**, 1873—1876).—An account is given of experiments carried out on cats and rabbits, poisoned by the hypodermic injection of morphine into the mesenteric circulation, to ascertain the amount of alkaloid in the different organs after death, the amount of alkaloid which could be recovered, and the extent to which the results of extraction are affected by cavity and arterial injection of formaldehyde as an embalming fluid.

It was found that if the analysis is commenced very soon after the death of the animal, 97·5% of the morphine injected can be extracted by Autenrieth's modification of the Stas-Otto process. The presence of formaldehyde has no appreciable effect on the results.

In the case of cats, the morphine was found in largest quantity in the urine, whilst the organs, arranged in order of morphine content, were liver, kidneys, spleen, and stomach. In the case of rabbits the order was kidneys, liver, urine, spleen, and stomach.

The percentages of morphine recoverable from the corpse decrease with time; thus, in the case of the cat, 72·5% was obtained one month after death and 68·5% three months after death. The loss of morphine from the corpse proceeds in two stages, with an intervening period during which the morphine content is fairly constant. The loss during the first stage is due to the decomposition of the free alkaloid present, and the loss during the second stage to decomposition of the morphine, which has combined with

some cell constituent, and thus escaped the preliminary decomposition. The secondary decomposition is greatly retarded by the presence of formaldehyde. E. G.

Chemistry of Vegetable Physiology and Agriculture.

Biochemistry of Micro-organisms. X. Formation and Fermentation of Formic Acid by Bacterium Coli. HARTWIG FRANZEN and HEINRICH KAHLENBERG (*Zeitsch. physiol. Chem.*, 1916, **97**, 314—324).—When *B. coli* from various sources are placed in suitable circumstances, the rate of production and subsequent fermentation of formic acid is the same in each case. H. W. B.

Action of Phosphates on Alcoholic Fermentation at Different Concentrations of Hydroxyl Ions. H. EULER and T. THOLIN (*Zeitsch. physiol. Chem.*, 1916, **97**, 269—278).—If a fermenting mixture of yeast and dextrose is maintained just alkaline to phenolphthalein by the repeated introduction of small quantities of sodium hydroxide, the addition of phosphate, instead of accelerating the rate of fermentation, diminishes it in proportion to the amount added. The same phenomenon occurs when a dry yeast preparation is employed. H. W. B.

The Total Destruction of Pentoses During Alcoholic Fermentation. H. PELLET (*Compt. rend.*, 1916, **163**, 274—276).—If a mixture of 200 grams of beetroot molasses and 1—2 grams of arabinose or xylose in 1 litre of water is fermented by 5—10 grams of top or bottom yeast at 28—32°, after two to two and a-half days, when all action has ceased, it is found that 10—20% of the pentose has disappeared. If, instead of using only one lot of yeast, a fresh amount of 5 grams is added each day, it is found that the whole of the pentose has disappeared. By increasing the amount of yeast added at the first to such an extent that fermentation is complete at the end of twenty-four hours, none of the pentose is decomposed, but during a further lapse of time the pentose slowly disappears. With cane-sugar molasses the fermentation must be carried out in such a way as to be complete at the end of six to twelve hours, or there may be loss of any pentose present. By this method the author has proved the presence of a reducing sugar, probably glutose, present in cane-sugar molasses which is not acted on by yeast, whatever be the amount used or the duration of its action. W. G.

Chemical Composition and Formation of Enzymes. XII. HANS EULER and ERIK LÖWENHAMM (*Zeitsch. physiol. Chem.*, 1916, **97**, 279—290).—The fermentation of pyruvic acid by yeast is acceler-

ated in the presence of antiseptics, such as toluene and chloroform, provided the yeast is fresh. When the yeast is dried, it still ferments pyruvic acid, but the addition of toluene or chloroform does not increase, and sometimes inhibits, the rate of fermentation. Drying the yeast greatly diminishes its fermenting power over dextrose, but not over pyruvic acid.

The invertase content of yeast is increased as much by previous fermentation with pyruvic acid as by treatment with sucrose or mannose (compare Euler and Cramér, A., 1914, i, 364).

H. W. B.

The Antagonistic Action of Salts in Plants. J. G. Maschhaupt (*Chem. Zentr.*, 1916, i, 1079; from *Verslag. Landbouwkund. onderzoek. Rijkslandbouwproefstat.*, 1916, **19**, 60 pp.).—In these experiments natural conditions were attained by growing the plants (maize) in earth contained in pots with perforated bottoms through which the roots passed into the prepared solutions below. Under these conditions solutions of the chlorides of sodium, potassium, and magnesium, and magnesium sulphate, above certain concentrations, were strongly poisonous, calcium chloride to a much less extent. Even with concentrations of $3/25M$ the toxic action of sodium and potassium chlorides was removed by the addition of only 10 c.c. of calcium chloride solution ($3/25M$) to 1138 c.c. of their solutions; the magnesium solutions required considerably more. The antagonism found by Osterhout between sodium and potassium chlorides, and between sodium chloride and magnesium sulphate was not confirmed with certainty, and in any case it is very small compared with that of calcium chloride. The calcium salts have a special function which can be undertaken by no other salt. The work of other investigators on this point, in particular that of Loew and Hansteen, is discussed. The contradictions there found may be explained on the ground that these authors drew their conclusions from quite different plant types, and it is not permissible to generalise on results obtained from one species, any more than to assume any parallelism in the antagonistic salt action in plants and animals. A feature common to all antagonistic action, however, is that it is a colloidal reaction, and the calcium ion undoubtedly has a special function in this respect, both in the animal and vegetable kingdoms. In practical agricultural investigations, when the plants are growing in the natural soil, great difficulties, underestimated by Loew and his collaborators, are experienced, particularly since sufficient knowledge is lacking of the way in which the roots exert their functions. G. F. M.

Osmotic Pressure in Plants. VI. Composition of the Sap in the Conducting Tracts of Trees at Different Levels and at Different Seasons of the Year. Henry H. Dixon and W. R. G. Atkins (*Sci. Proc. Roy. Dublin Soc.*, 1916, [ii], **15**, 51—62).—During the late autumn and winter the osmotic pressure of the wood sap of deciduous trees is small and approximately constant throughout; the pressure is, however, slightly greater in the stems,

roots, and upper portions than in the intervening portions. During the early spring, the sap obtains large amounts of sugars from the storage cells of the wood parenchyma, and the osmotic pressure shows a marked increase from root to summit, especially in the upper regions. In the late spring, the concentration of sugars is still considerable, being about half the earlier value, whilst the electrolytes are in much greater concentration than in the early spring.

A good deal of sucrose was found in *Acer macrophyllum*, whilst reducing sugars occur only in traces in the wood sap. Both reducing sugars and sucrose (the latter usually predominating) were found in the other trees examined. During the vernal mobilisation of reserves, the reducing sugars consist of hexoses and maltose; at other times maltose is absent.

In evergreens and sub-evergreens the gradients of osmotic pressure from root to summit are less regular than in deciduous trees.

N. H. J. M.

Rôle of Glucosides in Plants. A. GORIS (*Chem. Zentr.*, 1916, i, 850; from *Bull. Sci. Pharmacol.*, 1915, **22**, 99—110).—The author considers that the glucosides may be regarded as a form of mobilisation of the waste products of the plant metabolism. The phenolic residues which are harmful to the plant are rendered soluble by combination with the dextrose, and are transferred osmotically to the peripheral portions of the cortex. In the second place, the glucosides on decomposition yield sugars for food materials, whilst the liberated phenol component may be oxidised and furnishes the phlobaphen and the various autumnal colouring matters of the leaves. The function of the glucosides as foodstuffs for the plant is reduced, therefore, to a utilisation of the carbohydrate portion of the molecule, and is always of minor importance.

G. F. M.

Rôle of Glucosides in Plants. J. VINTILESCO (*Chem. Zentr.*, 1916, i, 851; from *Bul. Şoc. Ştiinţe Bucureşci*, 1915, **17**, 128—138).—A criticism of the work of Goris (preceding abstract). Investigations of the deposition of glucosides in plants, and of the artificial feeding of moulds with glucosidal solutions do not admit of conclusions being drawn as to the functions of glucosides. Moreover, the changes in the glucosidal content indicated by Bourquelot's biochemical method, and particularly the decrease, in the course of vegetation, and during the drying of plants, point to an opposite conclusion to that of Goris, namely, that the glucosides are substances which are utilisable to a certain extent, or at certain times, by the plants which produce them.

G. F. M.

Chemistry and Physiology of the Leaves of the Betel-Vine (Piper Betle) and of the Commercial Bleaching of Betel-Vine Leaves. II. HAROLD H. MANN and V. G. PATWARDHAN (*Mem. Dept. Agric. India, Chem. Ser.*, 1916, **4**, 281—322).—Analyses of the leaves were made at different dates and at different times on

the same day. The essential oil of the leaves, and the bleaching process were also investigated.

The value of the leaves seems to depend chiefly on the amount and character of the essential oil, which consists of a mixture of phenols and terpene-like compounds. As regards phenols, eugenol is the most prominent in Indian oils; betel-phenol is present in small amounts, whilst chavicol was not found. The best leaves are those which contain the greatest proportion of phenols.

Bleaching should be carried out in the dark, and preferably at a temperature of 29—33°. N. H. J. M.

Composition of the Fruit of Cicer Arietinum, L. AS. ZLATAROFF (*Zeitsch. Nahr. Genussm.*, 1916, **31**, 180—183).—The dry substance of the fruit of *Cicer arietinum*, L. (chick pea), contained: Fat. 6·30; starch, 50·32; crude fibre, 3·62; ash, 2·87; total nitrogen, 3·34; protein nitrogen, 2·11; nuclein nitrogen, 0·10; ammonia nitrogen, 0·10; amide nitrogen, 0·01; amino-acid nitrogen, 0·12; total phosphoric acid, 0·998; lecithin phosphoric acid, 0·142; protein phosphoric acid, 0·486; inorganic phosphoric acid, 0·118%; organic, soluble phosphoric acid, 0·244%. Oxalic acid (0·007%); citric acid, betaine, and choline (0·02%); adenine, inositol, and an isomeride of phytosterol were also present. The latter, *slanutosterol*, was present in the fat to the extent of 0·3%; its acetate had m. p. 128°. W. P. S.

Lichens and their Characteristic Constituents. XIV. Use of Lichens as Provisions and Fodder. O. HESSE (*J. pr. Chem.*, 1916, [ii], **93**, 254—270).—The author calls attention to the fact that in various parts of the world certain lichens have long been used as articles of food for man and beast.

Equal weights of potatoes and Iceland moss (*Cetraria islandica*) or reindeer moss (*Cladonia alpestris*) have been separately submitted to the same hydrolytic treatment with 6 or 8% sulphuric acid and the resulting sugars estimated. The lichens yield about three times as much sugar (chiefly dextrose from *C. islandica* and *d*-galactose from *C. alpestris*) as the potato.

Directions are given as to the collection of the lichens and the treatment necessary to render them fit for human consumption. C. S.

Notes on Plant Chemistry. P. Q. KEEGAN (*Chem. News*, 1916, **114**, 74—75).—Analyses, organic and mineral, of (1) *Parmelia saxatilis*, (2) *Primula vulgaris*, (3) *Rumex sanguineus*, and (4) *Narcissus pseudonarcissus*. The total ash amounted to: (1) 5·4%; (2) 14·9%, and (3) 11·7%. The following analyses of the ashes are given:

	CaO.	MgO.	P_2O_5.	SO_3.	Cl.	SiO_2.
(1)	2·8	1·8	4·1	1·1	—	5·5
(2)	12·2	3·4	4·2	4·3	17·2	6·3
(3)	17·5	5·3	6·2	3·3	5·4	7·3
(4)	10·1	3·6	5·0	4·0	9·8	3·3

The ash of daffodil leaves contains considerable amounts of manganese. N. H. J. M.

Barium in Tobacco and other Plants. BONNIBEL ARTIS and HAROLD L. MAXWELL (*Chem. News*, 1916, **114**, 62—63).—Estimations of barium in tobacco from Cuba, Sumatra, and from different parts of the United States, and in a number of mature and immature leaves from shrubs and trees.

In tobacco leaves the barium sulphate varied from 0·0132 to 0·0980%, and in the stems from 0·0280 to 0·504%.

The smallest amounts of barium in mature leaves were found in wild olive ($BaSO_4 = 0·0048\%$) and the highest in walnut leaves (0·0752%). Immature leaves contained from 0·0071% (sumac) to 0·0941% (wild grape). The soil on which the trees or shrubs were grown gave 0·1312% of barium sulphate. N. H. J. M.

Fruit of Vaccinum Corymbosum [Huckelberry]. CHARLES H. HARRIS and WILLARD D. THRAMS (*Chem. News*, 1916, **114**, 73).—The dried fruit contained 0·7% of nitrogen, 41·46% of laevulose, tartaric acid, and a trace of citric acid. The ash contained K_2O, 5·65; Na_2O, 2·26; CaO, 18·11; MgO, 11·48; Al_2O_3, 17·39; Fe_2O_3, 10·50; MnO, 0·35; P_2O_5, 14·36; SO_3, 10·94; and SiO_2, 6·33%.

N. H. J. M.

Soil Colloids. I. Flocculation of Soil Colloid Solutions. M. I. WOLKOFF (*Soil. Sci.*, 1916, **1**, 585—601).—The flocculating effect of the same electrolyte varies with different soil solutions, depending largely on the chemical composition of the soils. For the flocculation of a more concentrated soil, a greater amount of electrolyte is required than in the case of less concentrated solutions.

In soil colloidal solutions the flocculation reaction follows the law of mass action. N. H. J. M.

Oxidation of Sulphur in Soils as a Means of Increasing the Availability of Mineral Phosphates. JACOB G. LIPMAN, HARRY C. MCLEAN, and H. CLAY LINT (*Soil Sci.*, 1916, **1**, 533—539). —Sulphofication experiments in which weekly (later fortnightly) estimations of acidity and of soluble phosphoric acid were made in soils alone, in soils + sulphur, in soils + rock phosphate, and in soils + sulphur and rock phosphate. The soils employed were pure sea sand, a red silt loam, and a medium loam.

The results show that considerable amounts of sulphuric acid are formed from the sulphur and that the acid acts on insoluble phosphates with production of phosphoric acid available to crops. The character of the soil plays an important part in stimulating or retarding sulphofication. The best results were obtained in the red silt loam which, at the end of fifteen weeks, contained nearly 2 grams of citrate soluble and nearly 1 gram of water-soluble phosphoric acid, when 5 grams of sulphur and 15 grams of rock phosphate were added. In sand the amounts of soluble phosphoric acid produced were about one-fifth of the amounts in the red soil.

N. H. J. M.

Organic Chemistry.

Action of Aluminium Chloride on Petroleum. AIMÉ PICTET and (MME.) I. LERCZYNSKA (*Bull. Soc. chim.*, 1916, [iv], **19**, 326—334).—Following the work of Aschan (compare A., 1902, i, 749) on the action of aluminium chloride on aliphatic hydrocarbons, the authors have examined its effect on the fractions (b. p. above 140°) from petroleum from different sources. The anhydrous aluminium chloride was added to the petroleum, in which it dissolved, and the liquid, which turned brown, was then distilled, fractions being collected over the following ranges of temperature: 40—140°, 140—180°, 180—360°, residue. The first fraction, b. p. 40—140°, and the solid residue were particularly studied, the former being compared with "natural benzine" as regards its physical properties and its chemical constitution. A careful examination of this fraction showed that it consisted of about 35% of hydrocarbons, C_nH_{2n+2}, and 65% of cyclic hydrocarbons, C_7H_{14} and C_8H_{16}. The solid residue had the composition C_nH_n and closely resembled natural asphalt in its properties.

The most satisfactory amount of aluminium chloride to add is 10% of the weight of petroleum used. Of other chlorides tried, only ferrous and ferric chlorides could be used in place of the aluminium chloride, and these required a higher temperature.

W. G.

Recracking of a Cracked Oil Produced from Petroleum. GUSTAV EGLOFF and THOMAS J. TWOMEY (*J. Physical Chem.*, 1916, **20**, 597—620).—In the cracking of petroleum, either for gasolene or aromatic substances, a quantity of the cracked oil is recovered in the condensers. This oil is distilled up to a temperature of 170° when gasolene, or aromatic hydrocarbons, benzene, toluene, and xylene are obtained. The present paper deals with the treatment of the residue left after this distillation. A number of comparative experiments have been carried out in which petroleum and the residue obtained from it, as described above, have been cracked at various temperatures and pressures. It is shown that under identical conditions the cracked oil does not decompose to the same extent as the paraffin oil, and that the cracked oil is not so well adapted as the petroleum for either gasolene or aromatic hydrocarbon production. It is also shown that whenever cracking takes place to a lower boiling hydrocarbon from a cracked oil, this may be attributed to a large extent to the unchanged petroleum in the cracked oil, and not to its aromatic constituents. There is a limit to the number of times which an oil can be recracked, because the tendency of the reaction is to form aromatic compounds which decompose into neither gasolene nor members of the benzene series to an appreciable extent, but tend toward the ultimate products, carbon and hydrogen.

J. F. S.

The Time Factor in the Formation of Aromatic Hydrocarbons from a Paraffin Base Oil. G. EGLOFF and T. J. TWOMEY (*J. Soc. Chem. Ind.*, 1916, **35**, 1004; from *Met. Chem. Eng.*, 1916, **15**, 245—250).—The effect of the time factor or rate of oil flow has been studied in connexion with the formation of benzene, toluene, and xylene from a paraffin base oil. The oil was cracked at a constant temperature of 700° and at 68 kilos. pressure, the rates of flow being 54, 71, 104, 136, and 163 litres per hour respectively. As the time factor increased, that is, with a diminished rate of oil flow, the percentage of recovered oil decreased from 65·5 to 17·5, and the $D^{15 \cdot 5}$ of the oil increased from 0·879 to 0·978, the effects being similar to those produced by increasing the temperature of cracking. The maximum quantity of benzene in the recovered oil, namely, 26·3%, was obtained at the rate of 54 litres per hour, the formation of benzene increasing with decrease in the rate of flow of oil. The maximum percentages of toluene (13·8) and xylene (5·9) were both obtained at the rate of 71 litres per hour. Toluene and xylene showed an increase and then a decrease, whilst benzene increased continuously with the time factor. On the basis of oil used, the maximum proportion of benzene (6·6%) was obtained at 54 litres per hour, of toluene (4·1%) at 71 and 104 litres per hour, and of xylene (2·4%) at 104 litres per hour. The percentage of recovered oil distilling up to 170° increased with increase of the time factor to a maximum of 44·7% and then decreased, and the sp. gr. of the distillate increased to 0·875. The recovered oil obtained at the rate of 54 litres per hour yielded practically pure benzene, toluene, and xylene when fractionally distilled. No regularity was apparent in the distillation fractions above 170°, with the exception that the formation of tar or pitch decreased with increase in the rate of oil flow. Under the conditions of the experiments, a maximum yield of 57 litres of benzene, toluene, and xylene was obtained from 454 litres of oil used at the rate of 71 litres per hour at 700° and a pressure of 68 kilos. H. W.

A Highly Unsaturated Hydrocarbon in Shark Liver Oil. MITSUMARU TSUJIMOTO (*J. Ind. Eng. Chem.*, 1916, **8**, 889—896).—The liver oils obtained from two Japanese sharks, *Squalus mitsukurii* and *Deania eglantina*, contain 90·17% and 72·88% of unsaponifiable substances, respectively, of which 89·62% or 71·64% consists of a hydrocarbon, *squalene*, the remainder being cholesterol. This hydrocarbon has the formula $C_{30}H_{50}$; b. p. 262—264°/10 mm.; solidifying point, −75°; D_4^{15} 0·8587; n_D^{20} 1·4965; iodine number, 388·12; it possesses drying properties similar to those of the vegetable drying oils. W. P. S.

Preparation of Aluminium Alkyloxides. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 293613. Addition to D.R.-P., 286596; from *J. Soc. Chem. Ind.*, 1916, **35**, 1083).—The higher homologues of ethyl alcohol are caused to react with metallic aluminium in presence of a very small quantity of a mercuric salt.

The reaction may be started with a portion of the aluminium and the remainder added at intervals. The aluminium alkyloxides are soluble in the alcohols from which they are derived, and may be isolated in the pure state by crystallisation or by distilling off the alcohol. H. W.

Complex Borates. ADOLF GRÜN and H. NOSSOWITSCH (*Monatsh.*, 1916, **37**, 409—423).—The increased rotatory power of solutions of the polyhydric alcohols in presence of boric acid, and the increase in the degree of ionisation of the acid, are usually attributed to the formation of complex compounds containing the alcohol and the acid.

Such compounds containing mannitol, dulcitol, and sorbitol, and lithium or sodium metaborate, have been obtained in the free condition. The method employed consists in adding gradually the calculated quantity of the alkali carbonate to a concentrated solution containing boric acid and a large excess of the polyhydric alcohol. The separation of the complex compound is facilitated by the addition of ethyl or methyl alcohol.

The substances obtained in this way are *dimannitol-lithium metaborate*, $LiBO_2,2C_6H_{14}O_6,2H_2O$; *trimannitol-lithium metaborate* $LiBO_2,3C_6H_{14}O_6,2H_2O$; *trimannitol-sodium metaborate*,

$$NaBO_2,3C_6H_{14}O_6,5H_2O;$$

tridulcitol-sodium metaborate, $NaBO_2,3C_6H_{14}O_6,5H_2O$; *trisorbitol-lithium metaborate*, $LiBO_2,3C_6H_{14}O_6,2H_2O$. The ratio between the alcohol and the borate molecules is obviously independent of the nature of the metal and the constitution of the alcohol, but the proportion of water seems to be determined by the alkali metal. Attempts to isolate corresponding potassium compounds were unsuccessful, and a negative result was also obtained in the case of boric acid.

Although there can be little doubt that such compounds are present in solution, there is a considerable difference between solutions of the free acid and the alkali salts according to measurements of the rotatory power.

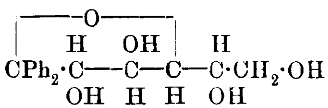
The rotatory power of solutions containing a fixed quantity of mannitol was found to be only slightly altered when the ratio of boric acid to mannitol was made equal to 1 : 1, 1 : 2, 1 : 3.

In similar experiments with sodium metaborate, the rotation was found to increase rapidly with the quantity of borate present. This would seem to indicate that one compound only is formed by the free acid, whilst the alkali borates give rise to three complex compounds. H. M. D.

Diaryl Derivatives of Sorbitol and Dulcitol. C. PAAL [with CARL KÜSTER and CARL ROTH] (*Ber.*, 1916, **49**, 1583—1597. Compare A., 1906, i, 400, 802; 1912, i, 31).—Some other *αα*-diaryl derivatives of dulcitol and sorbitol have been obtained and the acylation, anhydride formation, and oxidation of *αα*-diphenyldulcitol (formerly designated *αα*-diphenylgalactohexitol) are described.

Pure tetra-acetyl-*d*-gluconolactone, $[\alpha]_D^{20} + 94{\cdot}28°$, has been obtained from a specimen of *d*-gluconic acid purified through the *calcium* salt, $C_{12}H_{22}O_{14}Ca,H_2O$. This lactone reacts with magnesium *p*-tolyl bromide to form *αα-di-*p*-tolylsorbitol*, which crystallises in bundles of needles, m. p. 169·5—170°, $[\alpha]_D^{20} + 97{\cdot}1°$, and with magnesium benzyl chloride to give *αα-dibenzylsorbitol*, which separates in optically inactive, pointed prisms, m. p. 146—147°.

A pure specimen of tetra-acetylgalactonolactone, $[\alpha]_D^{20} - 8{\cdot}5°$, was also prepared through calcium *d*-galactonate. The *αα-diphenyldulcitol* which this lactone yields has $[\alpha]_D^{20} + 72{\cdot}9°$ in water, $+56{\cdot}23°$ in alcohol (*loc. cit.*), and $+76{\cdot}4°$ in ethyl acetate, and forms a *βγδεζ-penta-acetate*, needles, m. p. 151°, $[\alpha]_D^{20} + 14{\cdot}6°$, and a *dibenzoate*, m. p. 172—173°, $[\alpha]_D^{18} + 64{\cdot}7°$. On oxidation with permanganate, it yields benzophenone and other substances which have not been identified, and on warming with dilute acids it forms an internal anhydride, apparently a *3:4-dihydroxy-2:2-diphenyl-5-αβ-dihydroxyethyltetrahydrofuran* (annexed formula), which crystallises from water in large, transparent tablets with $4H_2O$, m. p. 75—92°, $[\alpha]_D^{20} - 108{\cdot}6°$, or from alcohol, after drying at 105°, as a white crust, m. p. 108—111°, $[\alpha]_D^{20} - 82{\cdot}1°$.



*αα-Di-*p*-tolyldulcitol*, needles, m. p. 194—196°, $[\alpha]_D^{20} + 49{\cdot}45°$ (alcohol), $+59{\cdot}68°$ (30% acetic acid), $+68{\cdot}44°$ (90% acetic acid), $+58{\cdot}76°$ (glacial acetic acid), and *αα-dibenzyldulcitol*, nodules of needles, m. p. 182—184°, $[\alpha]_D^{20} + 1{\cdot}46°$ (alcohol), are prepared from the same lactone by the action of the appropriate Grignard agent.

A table is given which summarises the values of $[\alpha]_D$ for dextrose, *d*-galactose, and *l*-arabinose, and their corresponding alcohol-acids, lactones, acetyl-lactones, αα-diphenyl-, -di-*p*-tolyl-, and -dibenzyl alcohols, and anhydro-compounds of the αα-diphenyl alcohols, and the influences of various groupings are briefly discussed. J. C. W.

Amidic Hydrolysis of Fats. E. DE' CONNO and R. BIAZZO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1915, [iii], **21**, 322—327).—Various vegetable drying, semi-drying, and non-drying oils, animal oils, and solid fats have been hydrolysed by heating with an equal weight of aniline in a sealed tube in a Carius oven at 230° for five hours. The anilides thus obtained melt to dark red liquids, and solidify at temperatures varying from 24·7° to 38·3° for those from the oils, and from 55° to 60° for those from the solid fats. Hydrolysis never proceeds to completion under these conditions, but the identity of the acids obtained by hydrolysis of the anilides with those given by hydrolysis of the original fats shows that the constituent acids of a fat are represented in the anilides integrally and in their original proportions. Thus, amidic hydrolysis may be utilised for the identification of the constituent acids of different fats, and possibly also for the determination of such constituents. T. H. P.

Hydroxy-acids: Transformation of Erucic Acid into Hydroxybehenic Acid. AD. GRÜN and JOS. JANKO (*Chem. Zentr.*, 1916, i, 1139—1140; from *Chem. Umschau Fett Harz-Ind.*, 1916, **23**, 15—20. Compare Shukov and Schestakov, A., 1908, i, 755).—The preparation of erucic acid from the fatty acids of rape oil by means of the lead salt does not give good results, fractionation of the methyl esters of these acids being far more successful.

Treatment of erucic acid with sulphuric acid appears to yield an ester of hydroxybehenic acid with erucic acid, a molecule of sulphuric acid being added and then liberated: $C_{21}H_{41}\cdot CO_2H + SO_3H\cdot O\cdot C_{21}H_{42}\cdot CO_2H = H_2SO_4 + C_{21}H_{41}\cdot CO\cdot O\cdot C_{21}H_{42}\cdot CO_2H$ (I); this esterification proceeds to completion when 2 mols. of sulphuric acid are taken per 1 mol. of erucic acid. Whether lactones are formed during the reaction is uncertain. Hydrolysis of the above ester yields *hydroxybehenic acid*, $CH_3\cdot[CH_2]_7\cdot C_2H_3(OH)\cdot[CH_2]_{11}\cdot CO_2H$, which forms white crystals, m. p. 89—90°.

When hydroxybehenic acid is distilled at 7 mm. pressure, water is lost and erucic acid formed, together apparently with a less fusible isomeric acid. If hydroxybehenic acid is heated until the loss in weight corresponds with $1H_2O$, a viscous oil is obtained which yields hydroxybehenic acid when hydrolysed with alcoholic potassium hydroxide, and appears to be an anhydride of the type of the estolides, $C_nH_{2n}(OH)\cdot CO\cdot[O\cdot C_nH_{2n}\cdot CO]_m\cdot O\cdot C_nH_{2n}\cdot CO_2H$ (compare Grün and Wetterkamp, *Zeitsch. Farbenind.*, 1909, **8**, 279). By the action of sulphuric acid on hydroxybehenic acid, half of the latter is converted into the unsaturated erucic or *iso*erucic acid, the remainder yielding the ester (I); no behenolactone could be found.

The following derivatives of hydroxybehenic acid were prepared: *Sodium* and *potassium* salts; *ethyl* ester, m. p. 49·5°; *methyl* ester, microscopic crystals, m. p. 53°. The *acetyl* derivative of the methyl ester, $C_{21}H_{42}(OAc)\cdot CO_2Me$, loses acetic acid quantitatively when distilled in a vacuum (2 mm.), yielding the *compound* $C_{21}H_{41}\cdot CO_2Me$; hydrolysis of this ester gives *iso*erucic acid, m. p. 54—56°. T. H. P.

Suberogenic Acids. F. SCURTI and G. TOMMASI (*Gazzetta*, 1916, **46**, ii, 159—168).—The suberogenic acids, which have been described under the names phellonic acid (see von Schmidt, A., 1904, i, 501), suberinic acid, and phloionic acid, are shown to be oxidation products of fatty acids, from which they are evidently formed by enzymic oxidation. Phellonic acid is α-hydroxybehenic acid, suberinic acid is ricinoleic acid, and phloionic acid a saturated, tricarboxylic, aliphatic acid containing 25 atoms of carbon in the molecule. On the basis of these results, cork must be regarded as formed by the intimate linking of a cellulosic substance, of hemicellulosic derivatives, and of oxidation products of fatty acids.

T. H. P.

Ethylenethioglycollic [Ethylenedithiolacetic] Acid and its Oxidation Products. ÅKE TIBERG (*Ber.*, 1916, **49**, 2024—2029. Compare A., 1914, i, 384).—An account of the ability of ethylene-

dithiolacetic acid to form metallic complexes has already been given. Some typical salts, esters, etc., are now described.

The value K_{25} is about 0·043, but rises with increasing dilution. The *sodium* salt, $C_2H_4(S{\cdot}CH_2{\cdot}CO_2Na)_2$, and the *sodium hydrogen* salt, are very soluble; the *potassium* salt forms rhombic tablets and the *potassium hydrogen* salt forms thin leaflets; the *calcium* salt crystallises in small prisms with $1H_2O$. The *methyl* ester has b. p. 190°/11 mm., D^{25} 1·2332, n_D 1·524; the *ethyl* ester has b. p. 195°/11 mm., D^{25} 1·1609, n_D 1·510. The *amide* is a granular mass, m. p. 175·5°; the *p*-toluidide has m. p. 204—205° (compare Beckurts and Frerichs, A., 1906, i, 652).

Oxidation with bromine water yields *ethylenedisulphoxyacetic acid*, $C_2H_4(SO{\cdot}CH_2{\cdot}CO_2H)_2,2H_2O$, small prisms, m. p. 138—139° (anhydrous), whilst permanganate oxidises the acid to *ethylenedisulphonylacetic acid*, $C_2H_4(SO_2{\cdot}CH_2{\cdot}CO_2H)_2$, which crystallises in thin leaflets, m. p. 195—196°, and forms a sparingly soluble *barium* salt and an *ethyl* ester, in small, white needles, m. p. 80—81°.

J. C. W.

Some Complex Compounds of Ethylenethioglycollic [Ethylenedithiolacetic] Acid. ÅKE TIBERG (*Ber.*, 1916, **49**, 2029—2039. Compare A., 1914, i, 384).—Some more complex compounds have been obtained by the interaction of certain metallic salts and ethylenedithiolacetic acid or its esters.

The *methyl* ester of dichloroethylenedithiolacetatoplato-acid, $C_2H_4(S{\cdot}CH_2{\cdot}CO_2Me)_2,PtCl_2$, is a yellowish-brown powder, m. p. 188·5°, and the *ethyl* ester forms microscopic, yellow needles, m. p. 153·5°. They are obtained by the interaction of the esters and potassium platinochloride.

Cupric chloride gives rise to *dichloroethylenedithiolacetatocupro-acid*, $C_2H_4(S{\cdot}CH_2{\cdot}CO_2H)_2,CuCl_2$, a pale green, somewhat hygroscopic mass, and its *methyl* ester, dark green crystals, and also to the *methyl* ester of *dichlorobis-ethylenedithiolacetatocupro-acid*, $[C_2H_4(S{\cdot}CH_2{\cdot}CO_2Me)_2]_2,CuCl_2$, brownish-green crystals. The *copper* salt of ethylenedithiolacetic acid crystallises with $1H_2O$ in very slender needles.

The *silver* salt, $C_2H_4(S{\cdot}CH_2{\cdot}CO_2Ag)_2$, is a yellow, insoluble powder which dissolves in an excess of the corresponding sodium salt, and from this solution sulphuric acid precipitates *bis-ethylenedithiolacetatoargenta-acid*, $[C_2H_4(S{\cdot}CH_2{\cdot}CO_2)_2]_2H_3Ag$, in small, colourless prisms. The *sodium* salt of this,

$$[C_2H_4(S{\cdot}CH_2{\cdot}CO_2)_2]_2Na_3Ag,10H_2O,$$

crystallises in large, stable tablets, and the silver is attracted to the anode on electrolysis.

Bis-ethylenedithiolacetatocupra-acid (*ibid.*) may be obtained by the interaction of cuprous chloride (1 mol.) and ethylenedithiolacetic acid (2 mols.) in methyl alcohol. The corresponding *sodium* salt, $[C_2H_4(S{\cdot}CH_2{\cdot}CO_2)_2]_2Na_3Cu,10H_2O$, is formed in colourless scales by neutralising the complex acid or by dissolving cuprous iodide in a solution of sodium ethylenedithiolacetate. Under other conditions, the cuprous haloids have dissolved in methyl- or ethyl-

alcoholic solutions of the acid to yield the following esters: *methyl* ester of *dichloroethylenedithiolacetatocupra-acid*,

$$C_2H_4(S\cdot CH_2\cdot CO_2Me)_2,Cu_2Cl_2,$$

colourless crystals, m. p. 146—147°, *ethyl* ester, m. p. 112—114°; *methyl* ester of *dibromoethylenedithiolacetatocupra-acid*, m. p. 176—177°, *ethyl* ester, microscopic prisms, m. p. 135—136°; *methyl* ester of *iodoethylenedithiolacetatocupra-acid*,

$$C_2H_4(S\cdot CH_2\cdot CO_2Me)_2,CuI,$$

m. p. 75—78° (viscous) and again at 127—128° (mobile), *ethyl* ester, m. p. 66—69° (viscous), 111—112° (mobile). J. C. W.

Preparation of Acetaldehyde from Acetylene. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 293070. Addition to D.R.-P., 292818; from *J. Soc. Chem. Ind.*, 1916, **35**, 1082).—Metallic mercury in the presence of dilute acid is used instead of the mercuric salt specified in the chief patents (A., 1915, i, 1050).

H. W.

The Formation of Methylglyoxal and Formaldehyde in Glycolysis. B. J. SJOLLEMA and (MLLE.) A. J. H. KAM (*Rec. trav. chim.*, 1916, **36**, 180—193).—To confirm the opinion of Windaus and Knoop (compare A., 1905, i, 381) as to the intermediate formation of methylglyoxal in the formation of methylglyoxaline from dextrose and ammoniacal zinc oxide, and the opinion of Neuberg (compare A., 1915, i, 939) as to the behaviour of dihydroxyacetone in alkali solution, the authors have prepared these compounds and examined their behaviour under similar conditions. When ammoniacal zinc oxide is added to an aqueous solution of methylglyoxal and formaldehyde, there is an immediate precipitation of the zinc compound of methylglyoxaline (compare Windaus and Knoop, *loc. cit.*). Dihydroxyacetone, on the other hand, under similar conditions, only very slowly yields this zinc compound, the action not being much more rapid if formaldehyde is also present. The reaction is slow in this case, owing to the slow intermediate formation of methylglyoxal.

A preliminary examination of the behaviour of dihydroxyacetone and methylglyoxal respectively towards hydrazine hydrate in alcoholic solution gave results which were opposed to Neuberg's views. W. G.

Action of Hydrogen Sulphide on Dextrose. WILHELM SCHNEIDER (*Ber.*, 1916, **49**, 1638—1643).—When a pyridine solution of dextrose is saturated with hydrogen sulphide, left for some days, and then evaporated under reduced pressure, care being taken all the while to exclude air (a device is described), a syrup is left which contains thio-derivatives of dextrose. On adding a pyridine solution of silver nitrate, treated with dry ammonia until a precipitate begins to be formed, and then diluting the whole with alcohol, a mixture of silver salts is obtained which closely resembles the silver salt of thioglucose obtained from thiourethane

glucosides and sinigrin (A., 1914, i, 669, 977). The mixture apparently consists of the salt *A* and the salt *B* in the proportion 2 : 1.

$$OH\cdot CH_2\cdot CH(OH)\cdot\overbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot CH}^{O}\cdot SAg$$
(*A*.)

$$OH\cdot CH_2\cdot CH(OH)\cdot\overbrace{CH\cdot CH(OH)\cdot CH(OH)\cdot CH}^{S}\cdot SAg$$
(*B*.)

J. C. W.

The Rotatory Powers of the α- and β-Alkyl-*d*-glucosides and Alkyl-*d*-galactosides. EM. BOURQUELOT (*Compt. rend.*, 1916, **163**, 374—377).—An examination of the specific rotatory powers of the α- and β-alkyl glucosides and galactosides obtained by biochemical synthesis shows that the β-glucosides and β-galactosides are all lævorotatory, the difference between the value for the β-glucoside and β-galactoside of the same alcohol being of the order of 32°. Similarly, the α-glucosides and α-galactosides are all dextrorotatory, the difference again between corresponding members being about 35°. Differences of the same order and in the same direction are to be noted between β-dextrose and β-galactose and α-dextrose and α-galactose respectively. W. G.

Ethylthioglucoside. WILHELM SCHNEIDER and JOHANNA SEPP (*Ber.*, 1916, **49**, 2054—2057).—When sugars are condensed with mercaptans under the influence of hydrochloric acid, they usually form mercaptals, and these may be reconverted into the sugars and metallic mercaptides by the action of salts of the heavy metals (Fischer, 1894). If, however, the mercaptals are treated with only one molecular proportion of the metallic salt, only one mercaptan residue is displaced. Thus, dextrose ethyl mercaptal and mercuric chloride react to form *ethylthioglucoside*, according to the equation $OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot CH(SEt)_2 + HgCl_2 = C_6H_{11}O_5\cdot SEt + SEt\cdot HgCl + HCl$. This crystallises in silky needles, m. p. 153°, $[\alpha]_D^{20}$ +120·8°, tastes bitter, does not reduce Fehling's solution, is stable towards alkalis, but hydrolysed by acids, and forms a *tetra-acetate* in stout, prismatic needles, m. p. 63°, $[\alpha]_D^{20}$ +155·2°. J. C. W.

Ethylaminochromi-compounds. II. Chloropentaethylaminochromic Salts. HJ. MANDAL (*Ber.*, 1916, **49**, 1307—1323. Compare this vol., i, 202).—In the earlier, preliminary note it was stated that chloropentaethylaminochromic chloride gives characteristic precipitates with several reagents. A fuller account of the chloride and of these other salts is now given.

Chloropentaethylaminochromic bromide, $[CrCl(NH_2Et)_5]Br_2$, is obtained from a solution of the chloride on the addition of hydrobromic acid or potassium bromide, in broad, red tablets or leaflets; the *iodide* forms small leaflets; the *platinichloride*, $XPtCl_6,2H_2O$, separates in silky, yellowish-brown, microscopic, stellar aggregates; the *platinibromide* is orange-yellow; the *aurichloride*, $X(AuCl_4)_2$, crystallises in yellow, microscopic needles; the *mercurichloride*,

$XHgCl_4$, forms red tablets or prisms; the *mercuribromide* separates in stellar masses of doubly refractive needles; two *mercuri-iodides* are described; $XHgI_4$ is red and $X_2Hg_3I_{10}$ yellowish-brown; the *stibichloride*, $XSbCl_5$, forms a mass of small red needles; the *bismuthichloride*, X_2BiCl_7, forms carmine-red, microscopic crystals.

The *nitrate*, $X(NO_3)_2$, is prepared by converting the chloride into the carbonate by means of silver carbonate, and adding concentrated nitric acid to the solution of this; it crystallises in red, doubly refractive needles. The *hydrogen sulphate*,

$$X(HSO_4)_2,2H_2O,$$

is prepared by the action of concentrated sulphuric acid on the chloride; it crystallises in long needles or prisms from water, and in anhydrous needles from alcohol; the crystals exhibit in a striking manner a feature common to all these salts, namely, that of spinning around irregularly as they dissolve. The neutral *sulphate*, XSO_4, is obtained by the action of silver sulphate on the chloride, but is so soluble that it is difficult to purify.

The *dithionate*, XS_2O_6, crystallises in various combinations of octahedra with hexahedra; the *pentasulphide* forms doubly refractive, microscopic double pyramids; the *dichromate* separates in golden-yellow, glistening, thin tablets; the *tetrathiocyanodiamminochromiate*, $X[Cr(NH_3)_2(SCN)_4]_2$, crystallises in microscopic, double pyramids; the *chromicyanide*, $X[CrC_6N_6]_2$, forms glistening, red leaflets; the *cobalticyanide*, $X[CoC_6N_6]_2$, is red; the *hydrogen ferricyanide*, $XHFeC_6N_6$, yellowish-brown.

J. C. W.

Preparation of Alkylamines. HUGO KRAUSE (*Chem. Zeit.*, 1916, **40**, 810).—The industrial reduction of nitrobenzene to aniline by means of iron and hydrochloric acid is carried out with only one-fortieth of the amount of acid necessary to convert the iron into ferrous chloride and leave the base free; the solution remains acid throughout, the aniline only partly decomposing the ferrous chloride, giving aniline hydrochloride, which has an acid reaction. Methylamine and ethylamine are, however, strong bases which form neutral hydrochlorides and decompose ferrous chloride with precipitation of ferrous hydroxide. It seemed, therefore, improbable that the reduction of nitromethane or nitroethane would take place to any great extent in presence of as little as one-fortieth of the proportion of acid corresponding with the equation $R\cdot NO_2 + 3Fe + 7HCl = NH_2R,HCl + 3FeCl_2 + 2H_2O$. Under these conditions, however, it is found that at a gentle heat (50—60°) the acid reaction of the mixture gives way to increasing alkalinity, the ammoniacal odour of the amine increasing in intensity at the same time; when filtered from the iron oxides, the liquid is almost entirely free from iron.

The theory suggested to explain the formation of aniline assumes that the nitrobenzene is reduced by ferrous chloride with the help of water, an iron oxychloride being formed which undergoes regeneration to ferrous chloride by the action of metallic iron.

This theory can scarcely hold for the reduction of the nitro-paraffins, since there can be no ferrous chloride in solution after the latter has become alkaline. Presumably the iron acts directly on the amine hydrochloride first formed as on ammonium chloride, the changes occurring being expressible by the equations $2(NH_2R,HCl) + Fe = 2NH_2R + FeCl_2 + H_2$ and $2NH_2R + FeCl_2 + 2H_2O = 2(NH_2R,HCl) + Fe(OH)_2$; thus, the hydrogen and the ferrous hydroxide may be regarded as the true reducing agents. This view is in agreement with the observation that nitro-paraffins are not reduced by iron and water alone, whereas reduction occurs on addition of a little of the amine hydrochloride.

In practice, when a high yield of the alkylamine is desired, sufficient acid should be present to keep the liquid acid, since the reduction proceeds slowly in the alkaline solution. An almost quantitative yield of methylamine is obtained when 1 mol. of nitromethane and 1·5 mols. of hydrochloric acid are heated at 70° for an hour; with nitroethane under similar conditions, rather longer is required. T. H. P.

***iso*Propylamine.** S. GABRIEL (*Ber.*, 1916, **49**, 2120—2123).—Not many substitution products of *iso*propylamine are known as yet, but a hydroxy- and a bromo-compound have now been obtained.

β-Oximinopropyl alcohol is reduced by means of sodium amalgam to *iso*propylamine and also to *hydroxy*iso*propylamine*,

$$OH\cdot CH_2\cdot CHMe\cdot NH_2,$$

which forms a *hydrochloride*, hygroscopic leaflets, m. p. 86—87·5°, a *platinichloride*, brownish-yellow, hexagonal leaflets, m. p. 198—199°, and a *phenylthiocarbamide*,

$$NHPh\cdot CS\cdot NH\cdot CHMe\cdot CH_2\cdot OH,$$

transparent, short, stout prisms or rhombohedra, m. p. 141—142°. The latter condenses to form 2-*anilino*-4-*methyl*-4 : 5-*dihydrothiazole*, $\begin{array}{l}CHMe\cdot N\\ |\\ CH_2{-}{-}S\end{array}\!\!>\!C\cdot NHPh$, in flat needles, m. p. 91°, when heated with fuming hydrochloric acid at 100°.

Hydroxy*iso*propylamine is converted into *bromo*iso*propylamine* by heating it with fuming hydrobromic acid. This base is characterised by a *picrate*, $CH_2Br\cdot CHMe\cdot NH_2,C_6H_3O_7N_3$, which forms yellow, rhombic plates, m. p. 145—146°. J. C. W.

[Aryl Esters of Tetra-alkyldiamino*iso*propyl Alcohol.] L. THORP (U.S. Pat., 1193634; from *J. Soc. Chem. Ind.*, 1916, **35**, 979).—The mono-salts of esters of αγ-tetra-alkyldiamino*iso*propyl alcohol behave as local anæsthetics, in particular the *monohydrochloride* of *αγ-tetraethyldiamino*iso*propyl benzoate*, colourless crystals, m. p. 130°. When heated with hydrochloric acid or sodium hydroxide, it yields benzoic acid and αγ-tetraethyldiamino-di*iso*propyl alcohol; with potassium carbonate solution, it gives the oily αγ-tetraethyldiamino*iso*propyl benzoate. H. W.

[Hydrochlorides of γ-Dialkylaminopropyl Alcohol.] E. A. WILDMAN and L. THORP (U.S. Pats., (*A*) 1193649, (*B*) 1193650, (*C*) 1193651; from *J. Soc. Chem. Ind.*, 1916, **35**, 979).—(*A*). The salts of the aryl esters of γ-dialkylaminopropyl alcohols possess anæsthetic action, but only slight toxicity compared with cocaine. *γ-Diethylaminopropyl cinnamate hydrochloride*, white needles, m. p. 137°, is prepared by mixing equivalent quantities of γ-diethylaminopropyl alcohol, dissolved in an inert solvent, such as benzene, ether, or acetone, and cinnamoyl chloride, and filtering the precipitate produced. The free *base* is a colourless oil, which is hydrolysed by hydrochloric acid or sodium hydroxide, yielding cinnamic acid and γ-diethylaminopropyl alcohol.

(*B*). *γ-Diethylaminopropyl anisate hydrochloride* forms white crystals, m. p. 129°. The free *base* is a colourless oil.

(*C*). *γ-Diethylaminopropyl* p-*toluate hydrochloride* is a white, crystalline substance; the free *base* is a colourless oil. H. W.

Chemical Compound of Hexamethylenetetramine and Calcium Chloride and Process Relating to Same. E. SAMSON (U.S. Pat., 1193474; from *J. Soc. Chem. Ind.*, 1916, **35**, 979).—Calcium chloride and hexamethylenetetramine are dissolved separately in alcohol; the solutions are mixed and allowed to crystallise. The product is a stable combination of the two substances and is free from water of crystallisation. H. W.

Synthesis of Optically Active Diaminoglycerol [βγ-Diaminopropyl Alcohol]. EMIL ABDERHALDEN and EGON EICHWALD (*Ber.*, 1916, **49**, 2095—2103).—The resolution of βγ-diaminopropyl alcohol into its optical antipodes, coupled with the preparation of active α-aminopropanediol (A., 1915, i, 210), completes the series of active and inactive amino-substitution products of glycerol.

A convenient method for the preparation of βγ-dibromopropyl methyl ether, b. p. 84°/15 mm., is described, whereby about 1·5 kilos. may be obtained from 1 kilo. of allyl alcohol. This ether reacts with alcoholic ammonia at 90—100° to give a number of unsaturated compounds and condensation products, but a small yield of the desired *βγ-diaminopropyl methyl ether*,

$$NH_2\cdot CH_2\cdot CH(NH_2)\cdot CH_2\cdot OMe,$$

may be isolated by fractional distillation. This is a powerful base, b. p. 165—180°, which forms a *hydrobromide*, m. p. 247°, and is hydrolysed by boiling with hydrobromic acid to i-*βγ-diaminopropyl alcohol hydrobromide*, m. p. 198°. The ether is resolved by fractional crystallisation of the bromocamphorsulphonates and distillation of the separate salts, and from the active ethers the active alcohols are obtained by hydrolysis with hydrobromic acid. The hydrobromides of the *active* ethers are as follows: *d*-form, m. p. 244°, $[\alpha]_D^{18}$ +9·04°, *l*-form, m. p. 243°, $[\alpha]_D^{18}$ −5·82°; the hydrobromides of the *active* βγ-diaminopropyl alcohols are as follows: *d*-, m. p. 198°, $[\alpha]_D^{18}$ +5·20°, *l*-, $[\alpha]_D^{18}$ −1·99°.

The hydroxyl group can be replaced by treatment with fuming hydrobromic acid at 140—150°. i-*α-Bromopropylene-βγ-diamine*

hydrobromide, $CH_2Br\cdot CH(NH_2)\cdot CH_2\cdot NH_2,2HBr$, decomposes at 242°, and the d-*salt* has $[\alpha]_D^{18} + 7\cdot 27°$. J. C. W.

An Extension of the Theory of Addition to Conjugated Unsaturated Systems. II. The *C*-Alkylation of Certain Derivatives of β-Aminocrotonic Acid and the Mechanism of the Alkylation of Ethyl Acetoacetate and Similar Substances. ROBERT ROBINSON (T., 1916, **109**, 1038—1046. Compare this vol., i, 836).—The ready hydrolysis of ethyl β-aminocrotonate and its derivatives in acid solution is probably due to the alteration in position of the double linking during the formation of the salt, as represented by the scheme $NH_2\cdot CMe\!:\!CH\cdot CO_2Et + HCl \longrightarrow NH_2Cl\!:\!CMe\cdot CH_2\cdot CO_2Et \longrightarrow O\!:\!CMe\cdot CH_2\cdot CO_2Et + NH_4Cl$. This explanation accords well with the observation of Collie (*Annalen*, 1884, **226**, 316) that ethyl iodide and ethyl β-aminocrotonate yield a reaction product which, after treatment with ether (presumably moist), contains ethyl α-acetylbutyrate and ammonium iodide, the probable course of the reaction being $NH_2\cdot CMe\!:\!CH\cdot CO_2Et + EtI \longrightarrow NH_2I\!:\!CMe\cdot CHEt\cdot CO_2Et \longrightarrow O\!:\!CMe\cdot CHEt\cdot CO_2Et + NH_4I$. Ethyl β-diethylaminocrotonate also yields additive products with methyl and ethyl iodide, subsequent decomposition with water giving rise to diethylamine hydriodide with ethyl α-acetylpropionate and α-acetylbutyrate respectively, the change being representable: $NEt_2\cdot CMe\!:\!CH\cdot CO_2Et + MeI \longrightarrow NEt_2I\!:\!CMe\cdot CHMe\cdot CO_2Et + H_2O \longrightarrow O\!:\!CMe\cdot CHMe\cdot CO_2Et + NH_2Et_2I$. In view of these results, the successful methylation of ethyl β-aminocrotonate in ethereal solution by first forming a sodium derivative, and subsequently treating this with methyl iodide (Conrad and Epstein, A., 1888, 253), probably proceeds in the following manner: $NH_2\cdot CMe\!:\!CH\cdot CO_2Et \longrightarrow NHNa\cdot CMe\!:\!CH\cdot CO_2Et + MeI \longrightarrow NHNaI\!:\!CMe\cdot CHMe\cdot CO_2Et \longrightarrow NaI + NH\!:\!CMe\cdot CHMe\cdot CO_2Et \longrightarrow NH_2\cdot CMe\!:\!CMe\cdot CO_2Et$.

In confirmation of the views now put forward, it was desirable to realise experimentally the introduction of an alkyl group to a carbon atom not itself attached to hydrogen, which would dispose of the obvious alternative explanation involving a reactive hydrogen atom. *Methyl ethylenebis-β-amino-α-methylcrotonate*, $C_2H_4(NH\cdot CMe\!:\!CMe\cdot CO_2Me)_2$, pearly leaflets, m. p. 126°, was therefore prepared by the condensation of ethylenediamine and methyl α-acetylpropionate in methyl-alcoholic solution, and was submitted to successive treatment with methyl iodide and water, when the expected methyl α-acetyl*iso*butyrate was obtained together with other substances; the change is represented:

$$C_2H_4(NH\cdot CMe\!:\!CMe\cdot CO_2Me)_2 + 2MeI \longrightarrow C_2H_4(NHI\!:\!CMe\cdot CMe_2\cdot CO_2Me) + 2H_2O \longrightarrow C_2H_4(NH_3I)_2 + 2COMe\cdot CMe_2\cdot CO_2Me.$$

It is possible that unsaturated elements other than nitrogen can be conjugated with an ethylene linking, and the difficulty of the explanation of the alkylation of ethyl acetoacetate is removed by this conception, according to which the progress of the change will be represented by the stages $ONa\cdot CMe\!:\!CH\cdot CO_2Et + MeI \longrightarrow ONaI\!:\!CMe\cdot CHMe\cdot CO_2Et \longrightarrow COMe\cdot CHMe\cdot CO_2Et + NaI$. Since

the free enols generally do not undergo alkylation, it is necessary to assume that the unsaturated nature of the oxygen atom is increased by its union with a highly positive atom. Other abnormal reactions, such as the conversion of dimethylpyrone into a methiodide, which is actually a methoxy-compound (Baeyer, A., 1910, i, 763), are also capable of explanation by the assumption of a conjugated system, which in the case of dimethylpyrone is of the type ·O·C:C:C:O.

There appear to be many directions in which this theory of conjugated unsaturated centres may be extended, and in the original a few of the more interesting and promising problems are indicated.

D. F. T.

Reaction between Amino-acids and Carbohydrates as a Probable Cause of Humin Formation. M. L. Roxas (*J. Biol. Chem.*, 1916, **27**, 71—93).—The following percentages of amino-acids when boiled with a carbohydrate and hydrochloric acid are apparently transformed into humin: tryptophan, 71; tyrosine, 15; cystine, 3·1; lysine, 2·6; arginine, 2·3, and histidine, 1·8. The author suggests that condensation occurs between the amino-acid and the furfuraldehyde produced by the action of the acid on the carbohydrate, resulting in the production of a ring compound.

H. W. B.

Compounds Containing Hydrogen Peroxide of Crystallisation. H. Stoltzenberg (*Ber.*, 1916, **49**, 1545—1546).—Compounds with hydrogen peroxide should be more stable the lower their vapour pressures, and, therefore, isomorphous mixtures crystallising with hydrogen peroxide have been sought for. Such a *compound* is represented by the formula $CO(NH_2)_2,NaCl,\frac{1}{2}H_2O_2$.

The amino-group seems to play an important part in affixing hydrogen peroxide molecules. Alkylated or acetylated carbamides have no additive capacity. Biuret gives the *compound*

$$5C_2H_5O_2N_3,H_2O_2,$$

and alloxan the *compound* $10C_4H_2O_4N_2,H_2O_2$. Parabanic acid and allantoin do not crystallise with hydrogen peroxide, but allantoic acid gives the *compound* $C_4H_8O_4N_4,3H_2O_2$. J. C. W.

Imino-esters of the Thiocyanates. Angelo Knorr (*Ber.*, 1916, **49**, 1735—1740).—Thiocyanic esters combine with alcohols and hydrogen chloride to form the hydrochlorides of the esters of the iminoalkyl(aryl)thiolformic acids, thus: R·S·CN + R′OH + HCl = RS·C(OR′):NH,HCl. These are crystalline salts which are readily decomposed by water or heat into the alkyl chloride and alkylthiolformamide (aminothiolformic ester), thus:

$$RS{\cdot}C(OR'){:}NH,HCl = RS{\cdot}CO{\cdot}NH_2 + R'Cl.$$

For this reason, special precautions must be taken to exclude moisture during the preparation (a device is described), but the decomposition serves as a most convenient method for obtaining the alkylthiolformamides.

Ethyl iminomethylthiolformate hydrochloride,

$$SMe{\cdot}C(OEt){:}NH,HCl,$$

from equimolecular proportions of methyl thiocyanate, ethyl alcohol, and hydrogen chloride, crystallises in needles, decomp. 84—85°, and the free *ester*, obtained by shaking an ethereal suspension with potassium carbonate solution, is a stable, inflammable liquid, b. p. 56°/25 mm. *Ethyl iminoethylthiolformate hydrochloride*, from ethyl thiocyanate, forms needles, decomp. 74—75°; *ethyl iminophenylthiolformate hydrochloride* forms needles, decomp. 72—74°; iso*butyl iminophenylthiolformate hydrochloride*, from *iso*butyl alcohol and phenyl thiocyanate, decomposes at 109—110°, and the free *ester*, $SPh\cdot C(:NH)\cdot O\cdot C_4H_9$, is a mobile, inflammable liquid. The following salts were also prepared: *methyl iminomethylthiolformate hydrochloride*, prisms, decomp. 60—62°; *methyl iminoethylthiolformate hydrochloride*, decomp. 48—49°; *ethyl imino*iso*butylthiolformate hydrochloride*, decomp. 76°.

The alkylthiolformamides are prepared by heating the above salts on the water-bath. The alkyl iminomethylthiolformate salts give methylthiolformamide (methyl aminothiolformate),

$$SMe\cdot CO\cdot NH_2,$$

prisms, m. p. 107°; the alkyl iminoethylthiolformate salts yield ethylthiolformamide (thiourethane, ethyl aminothiolformate), $SEt\cdot CO\cdot NH_2$, large, white leaflets, m. p. 104°; the ethyl imino*iso*butylthiolformate salt gives ethyl chloride and *iso*butylthiolformamide (*iso*butyl aminothiolformate), glassy leaflets, m. p. 102°; and the phenylthiol derivatives yield phenylthiolformamide (phenyl aminothiolformate), $SPh\cdot CO\cdot NH_2$, m. p. 96—98°.

J. C. W.

Trithiocyanatoaquodiamminochromium A. WERNER [with J. A. SIEMSSEN] (*Ber.*, 1916, **49**, 1539—1544).—Nordenskjöld (A., 1893, i, 291) obtained a compound of the formula

$$Cr(NH_3)_2(SCN)_3,2H_2O$$

by oxidising Reinecke's salts of the type $[(NH_3)_2Cr(SCN)_4]R$. Both water molecules in this can be replaced by a thiocyanate residue on treatment with potassium thiocyanate, which indicates that the sixth co-ordination place is occupied by the double water molecule. One of these two molecules is displaced by many bases with the formation of salts, which are easily deprived of the bases again by the action of acids. The one water molecule is therefore assumed to be functioning as an acid, and the compound is the oxonium-like salt of this acid, thus: $\left[(NH_3)_2Cr{}^{(SCN)_3}_{OH}\right]H,H_2O$, whilst the salts with amines have the general formula

$$\left[(NH_3)_2Cr{}^{(SCN)_3}_{OH}\right]H,B.$$

Trithiocyanatoaquodiamminochromium is best obtained by adding concentrated hydrogen peroxide, freshly prepared by mixing sodium peroxide and concentrated hydrochloric acid in the cold, to Reinecke's salt. It separates from solution in water at 30—40° in large crystals. The *brucine* salt is a pale red precipitate; the

pyridine salt forms pearly leaflets; the *a-picoline*, *a-collidine*, and *quinaldine* salts are very similar.

The product obtained by adding aniline to the solution of the compound contains a part soluble in water, from which pyridine precipitates the above salt, together with an insoluble substance which is recognised as *trithiocyanatodiamminoanilinochromium*, $\left[(NH_3)_2Cr{(SCN)_3 \atop NH_2Ph}\right]$. The true aniline salt is the part which dissolves. J. C. W.

Electrolytic and Saponifying Process for Producing Nitrile Derivatives [Oxamide]. J. E. BUCHER (U.S. Pat., 1194354; from *J. Soc. Chem. Ind.*, 1916, **35**, 979).—Gaseous cyanogen is led under pressure into a bath of concentrated halogen acid or other catalytic agent, which is stirred continuously and heated to the temperature most favourable to the formation of oxamide.

H. W.

Organo-lead Compounds. II. Simple Lead Tetra-alkyls and their Halogen Substitution Products. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1916, **49**, 1415—1428. Compare this vol., i, 684).—When lead haloids are added to magnesium alkyl haloids for the preparation of lead tetra-alkyls, great difficulty is usually experienced in separating the desired compound from the accompanying unsaturated lead alkyls. This may be overcome by converting the crude mixture into the lead trialkyl haloid by the action of a halogen at about $-70°$ and treating this afresh with the magnesium alkyl haloid. Lead tetra-alkyls suffer replacement of one alkyl group by a halogen atom at the low temperature, whilst a second group is expelled at about $-20°$. The lead dialkyl dihaloids are very stable towards halogens.

Lead tetramethyl has m. p. $-27·5°$, b. p. 110°, D_4^{20} 1·9951, n_D^{20} 1·5128, $n_F - n_C^{20}$ 0·01881; lead tetraethyl has b. p. 83°/13 mm., D_4^{18} 1·6591, n_D^{18} 1·5218, $n_F - n_C^{18}$ 0·01750; *lead tetra*-n-*propyl* has b. p. 126°/13 mm., D_4^{20} 1·4419, n_D^{20} 1·5094, $n_F - n_C^{20}$ 0·01566. Lead trimethyl chloride crystallises in well-developed, long, stout needles which sublime at about 105°. *Lead dimethyl dichloride*, $PbMe_2Cl_2$, is a white powder which is almost insoluble in most organic solvents. From it, the white *sulphide*, and *iodide*, hexagonal, yellow leaflets, may be prepared. *Lead trimethyl bromide* forms stout, snow-white prisms or slender needles, m. p. 133°, and *lead dimethyl dibromide* is a white, microcrystalline powder. *Lead triethyl chloride* crystallises in very long, glassy needles, m. p. 172°, and *lead diethyl dichloride* in pearly leaflets or needles. *Lead triethyl bromide* forms very long needles, m. p. 103—104° (decomp.), and lead diethyl dibromide is decomposed by hot solvents. *Lead tri*-n-*propyl chloride* crystallises in strongly doubly refractive rods, m. p. 135°, and *lead di*-n-*propyl dichloride* in quadratic leaflets, decomp. 228°. J. C. W.

Organo-lead Compounds. III. Mixed Lead Tetra-alkyls of the Type $PbR_2R'_2$. GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1916, **49**, 1546—1550).—The lead dialkyl dihaloids described recently (preceding abstract) react with magnesium alkyl haloids to form the mixed compounds of the above type. It is essential that the lead dialkyl haloids should be applied in the finely divided condition in which they are first obtained, that is, without allowing them to dry, otherwise they do not react, but may suffer decomposition into simple lead tetra-alkyls or unsaturated lead alkyls.

*Lead dimethyldi-*n*-propyl*, $PbMe_2Pr_2$, from lead dimethyl dichloride and magnesium *n*-propyl chloride, has b. p. 77—78°/13 mm., $D_4^{24\cdot4}$ 1·6230, $n_D^{23\cdot1}$ 1·5062, $n_F - n_C$ 0·01679. *Lead dimethyldiisobutyl* has b. p. 95·5—96°/13 mm., $D_4^{20\cdot6}$ 1·5042, $n_D^{20\cdot4}$ 1·5023, $n_F - n_C$ 0·01585. *Lead dimethyldiisoamyl* has b. p. 122—123°/13 mm., $D_4^{20\cdot0}$ 1·4302, n_D^{20} 1·5005, $n_F - n_C$ 0·01485. *Lead dimethyldiethyl*, from lead diethyl dichloride and magnesium methyl chloride, has b. p. 51°/13 mm., D_4^{20} 1·7906, n_D^{20} 1·5177, $n_F - n_C$ 0·01785. *Lead diethyldi-*n*-propyl* has b. p. 105°/13 mm., D_4^{25} 1·5285, n_D^{25} 1·5127, $n_F - n_C$ 0·01654. *Lead diethyldiisobutyl* has b. p. 124°/13 mm., D_4^{22} 1·4455, n_D^{22} 1·5081, $n_F - n_C$ 0·01564. *Lead diethyldiisoamyl* has b. p. 142°/13 mm., D_4^{20} 1·3757, n_D^{20} 1·5041, $n_F - n_C$ 0·01473.

The compounds are all stable, colourless oils, and the yields are very good. J. C. W.

Some Hydrocarbons contained in Coal. AMÉ PICTET, L. RAMSEYER, and O. KAISER (*Compt. rend.*, 1916, **163**, 358—361).—Coal, when ground to nuts and extracted in a Soxhlet apparatus with benzene, yielded about 0·05% of its weight of a light brown, amorphous powder and 0·25% of its weight of a brown liquid. This brown liquid, when examined, was found to resemble closely the oil obtained by distilling the coal in a vacuum (compare A., 1914, i, 155; 1915, i, 512). It had the same odour and density and a very similar chemical composition, containing about 0·5% of basic substances, 2% of oxygenated substances with hydroxyl groups, the remainder consisting of a mixture of hydrocarbons, of which one-fourth were saturated and three-fourths unsaturated. The unsaturated hydrocarbons were methyl*cyclo*hexadiene, 1:3-dimethyl*cyclo*hexadiene, 1:3:5-trimethyl*cyclo*hexadiene, a hydrocarbon, $C_{10}H_{16}$, b. p. 180—182°, D^{20} 0·8482, n^{20} 1·4850, a hydrocarbon, $C_{11}H_{16}$, b. p. 200—202°, D^{20} 0·8745, n^{20} 1·4948, a hydrocarbon, $C_{14}H_{16}$, b. p. 236—238°, D^{20} 0·9593, n^{20} 1·5523°, and a hydrocarbon, $C_{13}H_{12}$, probably dihydrofluorene. From the mixture of saturated hydrocarbons, only one was definitely identified, namely, melene, but a number of fairly definite fractions were isolated, boiling over small ranges of temperature. The saturated hydrocarbons extracted by benzene and fractionated resembled, fraction for fraction, those obtained by distilling the coal at 450° in a vacuum, and are also identical with the naphthenes found by Mabery in Canadian petroleum. From these results, coal appears

to consist of solid hydrocarbon material impregnated with a liquid very similar to petroleum. The liquid portion of the coal, like most of the petroleums, has a feeble rotatory power. When separated into its components, it is found that none of the fractions of the unsaturated portion have any rotatory power, and of the saturated fractions only those boiling above 180° show any rotatory power. None of the fractions obtained by distilling the coal in a vacuum showed any signs of optical activity, probably owing to racemisation during the distillation. W. G.

Formation of Toluene by the Action of Anhydrous Aluminium Chloride on Xylene and Benzene. FRANZ FISCHER and HERMANN NIGGEMANN (*Ber.*, 1916, **49**, 1475—1482).—The authors have studied the conditions for the most productive degradation of xylene to toluene by the action of aluminium chloride. The best temperature is found to be that of the boiling xylene, whilst 2—4% of aluminium chloride is quite sufficient and two hours long enough for the purpose. Under these conditions, xylene gives an approximately 12% yield of toluene, and also benzene and polymethylated benzenes.

So-called "solvent benzene I" gives more volatile products but little toluene, whilst "solvent benzene II" gives no oils of lower boiling point. Benzene is decomposed by the energetic action of aluminium chloride, but without producing more than traces of toluene.

Experiments on xylene–benzene mixtures have also been carried out with the hope of transferring a methyl group from the one to the other, but this ingenious idea has not yet led to definite results. J. C. W.

Sulphonation of Organic Compounds. A. HEINEMANN (Brit. Pat., 12260; from *J. Soc. Chem. Ind.*, 1916, **35**, 1008).—The sulphonation of aromatic compounds can be effected with a weaker acid, in a shorter time and without carbonisation, if a small quantity of iodine is added. Thus benzene is completely converted into benzenemonosulphonic acid if heated and stirred under reflux during five hours with sulphuric acid and a small quantity of iodine; the latter can be recovered by adding water to the product and filtering. H. W.

Preparation of Salts of the Sulphonic Acids of Benzyl Chloride [ω-Chlorotoluenesulphonic Acids] and their Homologues. ROHNER & Co. (D.R.-P., 293319; from *J. Soc. Chem. Ind.*, 1916, **35**, 1055).—Dry salts of toluenesulphonic acids or their homologues suspended in an inert medium, such as carbon tetrachloride, tetrachloroethane, etc., are treated with chlorine, the reaction mixture being boiled under a reflux condenser during the operation. H. W.

Preparation of 5 : 8-Dichloro-1-nitronaphthalene. FARBENFABRIK VORM. F. BAYER & Co. (D.R.-P., 293318; from *J. Soc. Chem. Ind.*, 1916, **35**, 1055).—5 : 8-Dichloro-1-nitronaphthalene is obtained

by chlorination of α-nitronaphthalene in presence of a chlorine carrier.
H. W.

The Nitration of the Three Chloroacetanilides with Nitric Acid and of the Three Chloroanilines in Sulphuric Acid Solution. A. F. H. LOBRY DE BRUYN (*Rec. trav. chim.*, 1916, **36**, 126—166).—A quantitative study of the nitration of the three chloroacetanilides with nitric acid (D 1·495) at $-10°$, and of the three chloroanilines in solution in sulphuric acid (D 1·84) with a mixture of nitric acid (D 1·50) and sulphuric acid at $-20°$.

p-Chloroacetanilide when nitrated under the above conditions yields 100% of 4-chloro-2-nitroacetanilide. *o*-Chloroacetanilide yields 59·1% of 2-chloro-4-nitroacetanilide, 39·2% of 2-chloro-6-nitroacetanilide, and 1·7% of 2-chloro-5-nitroacetanilide. *m*-Chloroacetanilide gives 44·2% of 3-chloro-6-nitroacetanilide and 55·8% of 3-chloro-4-nitroacetanilide. From these results the ratios of the velocities of nitration caused respectively by the chloro- and acetylamino-groups are zero for the *p*-chloro-compound, 0·017 for the ortho-compound, and 0·109 for the meta-compound. In every case, therefore, the directing force of the acetylamino-group is very much greater than that of the chloro-group.

p-Chloroaniline, when nitrated under the above conditions, gives 98·2% of 4-chloro-3-nitro- and 1·8% of 4-chloro-2-nitro-aniline. *o*-Chloroaniline gives 100% of 2-chloro-4-nitroaniline. *m*-Chloroaniline gives 59% of 3-chloro-6-nitro-, 39% of 3-chloro-4-nitro-, and 2% of 3-chloro-5-nitro- with 3-chloro-2-nitro-aniline. A calculation of the ratios of the velocities of nitration caused respectively by the chloro- and amino-groups is uncertain in the case of the meta- and para-compounds and impossible in the case of the ortho-compound.
W. G.

Formation of Active Secondary Amino-acids from Halogeno-acids and Primary Amines. EMIL FISCHER and LUKAS VON MECHEL (*Ber.*, 1916, **49**, 1355—1366).—The *N*-methyl derivatives of *d*-alanine, *l*-leucine, and *d*-phenylalanine have recently been prepared by a method which leaves no room for doubt as to their structure, since no substitution at the asymmetric carbon atom was involved (A., 1915, i, 242). With these for comparison, it was proposed to prepare methylamino-compounds by the action of methylamine on *l*-α-bromopropionic acid, *d*-α-bromo*iso*hexoic acid, and *d*-α-bromophenylpropionic acid in order to see whether the substitution follows the same course, in the sterical sense, as it does when ammonia is applied to these acids. This is found to be the case, but it does not follow that the conversion of an optically active halogeno-acid into any amino-acid will always take the same course. With benzylamine, for example, it was considered likely that inversion might take place during the substitution, but the question could not be solved. The active *N*-benzylalanine and phenyl-*N*-benzylalanine could be prepared readily enough by this method, but not by the intervention of the toluenesulphonyl compounds, and their exact configuration is therefore undetermined.

l-N-*Methylalanine*, from *l*-α-bromopropionic acid, has $[\alpha]_D^{20}$ $-5{\cdot}92°$ in water, and is very similar to the *d*-isomeride (*ibid*). *l*-*N*-Methylleucine was obtained from *d*-α-bromo*iso*hexoic acid and *l*-phenyl-*N*-methylalanine from *d*-α-bromophenylpropionic acid.

The active N-*benzylalanine*, $C_7H_7{\cdot}NH{\cdot}CHMe{\cdot}CO_2H$, obtained from *l*-$\alpha$-bromopropionic acid, crystallises in very slender needles, m. p. about 270° (decomp.), $[\alpha]_D^{20}$ $-3{\cdot}4°$, and forms a pale blue *copper* salt, $C_{20}H_{24}O_4N_2Cu,2H_2O$. The active *phenyl*-N-*benzylalanine*, $C_7H_7{\cdot}NH{\cdot}CH(CH_2Ph){\cdot}CO_2H$, from *d*-$\alpha$-bromophenylpropionic acid, is a sparingly soluble powder, m. p. 225° (corr. decomp.), $[\alpha]_D^{18}$ $+17{\cdot}79°$, which forms a well-crystallised *nitrate* and a pale blue *copper* salt.

Ethyl p-*toluenesulphonylaminoacetate*, from ethyl glycine hydrochloride and *p*-toluenesulphonyl chloride, has m. p. 64—66°, and reacts with benzyl bromide and potassium hydroxide to form p-*toluenesulphonyl*-N-*benzylglycine*,

$$C_7H_7{\cdot}SO_2{\cdot}N(CH_2Ph){\cdot}CH_2{\cdot}CO_2H,$$

m. p. 141° (corr.), which is readily hydrolysed to *N*-benzylglycine (Mason and Winder, T., 1894, **65**, 189).

p-*Toluenesulphonyl*-d-*alanine ethyl ester*, from the free acid (*loc. cit.*), has m. p. 65—66°, $[\alpha]_D^{20}$ $-34{\cdot}2°$, and yields p-*toluenesulphonyl*-d-N-*benzylalanine*, $C_7H_7{\cdot}SO_2{\cdot}N(CH_2Ph){\cdot}CHMe{\cdot}CO_2H$, in crystals, m. p. 79—80°, $[\alpha]_D^{20}$ $-3{\cdot}80°$, which combine with $\frac{1}{2}$ mol. of xylene. The hydrolysis of this derivative is accomplished with difficulty, and the small amount of *N*-benzylalanine which can be isolated is inactive.

d- and *dl*-Leucine yield yellowish-red *perbromides* of the *hydrobromides*, $C_6H_{14}O_2NBr_2$, when ice-cold solutions in concentrated hydrobromic acid are treated with bromine. J. C. W.

The Nitration of Benzyldiethylamine. E. NOELTING and A. KREGCZY (*Bull. Soc. chim.*, 1916, [iv], **19**, 335—338).—When benzyldiethylamine is nitrated in sulphuric acid solution it yields approximately 35—40% of the meta-derivative, 40—45% of the para-derivative, and 15—20% of the ortho-derivative, the group $\cdot NEt_2$ thus exerting a marked orientating influence, although in the side-chain. If prepared in large quantities the three isomerides may be separated by fractional distillation under reduced pressure, and if in small quantities by conversion into their picrates, which have differing solubilities in alcohol. The isomerides may be prepared separately by the action of the corresponding nitrobenzyl chlorides on diethylamine.

o-*Nitrobenzyldiethylamine* has b. p. 175—177°/42 mm., and gives a *picrate*, m. p. 117°; m-*nitrobenzyldiethylamine* has b. p. 206—208°/42 mm., and yields a *picrate*, m. p. 161°; p-*nitrobenzyldiethylamine* has b. p. 219—221°, and gives a *picrate*, m. p. 131°. The relative solubilities of the picrates in alcohol are meta : para : ortho : : 1 : 2·4 : 5·83. W. G.

Some Dyes Derived from Aminobenzyldiethylamines. E. NOELTING and A. KREGCZY (*Bull. Soc. chim.*, 1916, [iv], **19**, 338—341).—The three nitrobenzyldiethylamines (compare preced-

ing abstract) are readily reduced by zinc or iron in acetic acid solution, giving the corresponding amino-compounds, which yield well-defined mono- and di-picrates. The bases are colourless oils, which can be distilled under reduced pressure, and are strongly basic, giving readily soluble salts with mineral acids.

o-*Aminobenzyldiethylamine*, b. p. 153—155°/42 mm., gives a *picrate*, m. p. 143—144°, orange crystals, and a *dipicrate*, m. p. 135°, yellow crystals.

m-*Aminobenzyldiethylamine*, b. p. 167—168°/42 mm., gives a *picrate*, m. p. 142°, and a *dipicrate*, m. p. 148°.

p-*Aminobenzyldiethylamine*, b. p. 165—166°/42 mm., gives a *picrate*, m. p. 109—110°, and a *dipicrate*, m. p. 130°.

With picryl chloride the bases give *picryl* derivatives,

$$C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4\cdot CH_2\cdot NEt_2.$$

The *ortho*-derivative is obtained in black crystals, m. p. 131°, and gives a *picrate*, m. p. 208°; the *para*-derivative is obtained in orange crystals, m. p. 102—103°, and gives a *picrate*, m. p. 183°. These picryl derivatives are basic, and dye cotton mordanted with tannin orange-yellow and golden-yellow respectively. They also dye silk and wool.

With fluorescein chloride aminobenzyldiethylamine gives a *rhodamine*, $CO_2H\cdot C_6H_4\cdot C{<}{\scriptstyle C_6H_3(NH\cdot C_6H_4\cdot CH_2\cdot NEt_2) \atop \scriptstyle C_6H_3(NH\cdot C_6H_4\cdot CH_2\cdot NEt_2)}{>}O\cdot Cl$, which is much more soluble than the corresponding compound obtained from toluidine, and dyes silk, wool, and cotton mordanted with tannin a reddish-violet. W. G.

Metaquinonoids. EUG. BAMBERGER (*Ber.*, 1916, **49**, 1257—1258. Compare A., 1915, i, 1055).—In referring to Lippmann and Fleissner's dinitro-*m*-aminophenol, m. p. 225°, the author wrongly ascribed the 4:6-configuration to it, overlooking the fact that Reverdin and Widmer (A., 1914, i, 166) had shown that the compound was more probably 2:4-dinitro-*m*-aminophenol. This is now definitely proved by converting it, through the ethyl ether, into 2:4-dinitroresorcinol, m. p. 145°. The correction has no influence on the theoretical discussion of the metaquinonoid question.

J. C. W.

Experiments on the So-called Migration of Atoms and Groups. I. The Nitration of *p*-Iodoanisole and other Iodophenolic Ethers. GERTRUDE MAUD ROBINSON (T., 1916, **109**, 1078—1091).—It is already known that the migration of chlorine from side-chain to nucleus, as observed when *N*-chloroacetanilides are treated with hydrochloric acid, is due to the formation of the acetanilide and chlorine, which react with the formation of the nucleus-substituted end-product, together with regenerated hydrochloric acid. Other examples of migration of a halogen atom from one position to another in the benzene nucleus, for example, during the nitration or halogenation of phenols, may be explained by the displacement of the halogen by the entering group and the re-entry in the new position. Thus *p*-iodoanisole on nitration yields 2-iodo-

4-nitroanisole (Reverdin, A., 1896, i, 475), and free iodine is formed to some extent during the reaction; the apparent difficulty that iodine is a somewhat inactive agent is removed by a demonstration that iodine does react with *p*-nitroanisole in nitric acid solution, forming the same 2-iodo-4-nitroanisole. Another indication of the liberation of iodine as a necessary stage in this nitration is the intermediate formation of a small quantity of 2:4-di-iodoanisole. In an analogous manner to its para-isomeride, *o*-nitroanisole also can be iodinated in nitric acid solution to *4-iodo-2-nitroanisole*, pale yellow prisms, m. p. 98°.

3-Iodo-o-tolyl methyl ether, $C_6H_3MeI\cdot OMe$, an oil, b. p. 200°/19 mm., obtained from 3-amino-*o*-tolyl methyl ether by the diazo-reaction, is converted by nitric acid at the ordinary temperature into *3-iodo-5-nitro-o-tolyl methyl ether*, $NO_2\cdot C_6H_2MeI\cdot OMe$, colourless, hair-like crystals, m. p. 83°, whereas the isomeric *5-iodo-o-tolyl methyl ether*, colourless plates, m. p. 79—80°, prepared from 5-amino-*o*-tolyl methyl ether, m. p. 92—93° (Hofmann and Miller, A., 1881, 592, give 52—53°) (*acetyl* derivative, needles, m. p. 158°), on nitration, also yields 3-iodo-5-nitro-*o*-tolyl methyl ether, which is likewise formed in the combined action of iodine and nitric acid on 5-nitro-*o*-tolyl methyl ether.

In an examination of the behaviour of the iodophenolic ethers with nitric acid it is found that the normal reaction constituting the first phase of the chemical change is the displacement of an iodine atom in the ortho- or para-position to the methoxyl group with formation of free iodine and a nitro-derivative. Thus, 4:5-di-iodoveratrole, m. p. 132° (Brüggemann, A., 1896, i, 356, gives m. p. 125°), on treatment with nitric acid yields successively *4-iodo-5-nitroveratrole*, $NO_2\cdot C_6H_2I(OMe)_2$, intense yellow needles, m. p. 151°, and 4:5-dinitroveratrole; in like manner, 2:5-di-iodoquinol dimethyl ether is converted under similar conditions into *2-iodo-5-nitroquinol dimethyl ether*, $NO_2\cdot C_6H_2(OMe)_2I$, bright yellow needles, m. p. 152°, and 2:5-dinitroquinol dimethyl ether; in order to moderate the action of the nitric acid, the introduction of the first nitro-group into each of these two di-iodo-compounds was effected in acetic acid solution.

3-Iodo-6-nitro-p-tolyl methyl ether, $OMe\cdot C_6H_2MeI\cdot NO_2$, long, flat needles, m. p. 118°, was prepared from 6-nitro-3-amino-*p*-tolyl methyl ether by means of the diazo-reaction. On treatment with fuming nitric acid some iodine was liberated, and the reaction product contained *3:6-dinitro-p-tolyl methyl ether*,

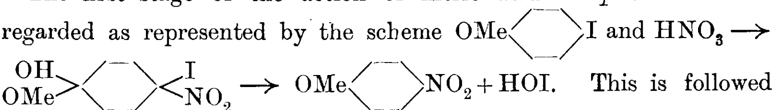
$$OMe\cdot C_6H_2Me(NO_2)_2,$$

pale yellow needles, m. p. 126°, together with *2:3:6-trinitro-5-hydroxy-p-tolyl methyl ether*, $OH\cdot C_6Me(NO_2)_3\cdot OMe$, yellow, rectangular prisms, m. p. 115°, which yielded a bright red *potassium* salt (needles) and gave bright yellow precipitates with the alkaloids, such as narcotine. When this trinitro-compound was treated with methyl sulphate in xylene solution in the presence of potassium carbonate, it was converted into *2:5:6-trinitrohomoveratrole*, $C_6Me(OMe)_2(NO_2)_2$, colourless needles, m. p. 73—74°. Attempts to prepare this by a different process were unsuccessful. *5:6-Dinitro-*

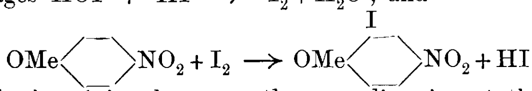
homoveratrole, $C_6HMe(OMe)_2(NO_2)_2$, colourless needles, m. p. 120°, produced by the nitration of 6-nitro-4-hydroxy-*m*-tolyl methyl ether, resisted attempts at further nitration; on reduction and condensation with phenanthraquinone it gave a deep yellow phenanthraphenazine.

In a discussion of the probable details of the mechanism of the "migration" the author considers that the iodine is most likely removed from the nucleus as hypoiodous acid, which then undergoes decomposition with formation of iodine and iodic acid, and also to some extent reacts with hydrogen iodide produced in the iodination, yielding iodine.

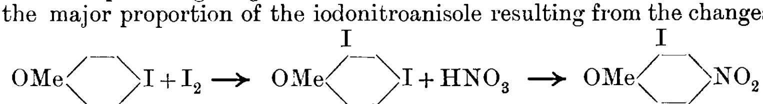
The first stage of the action of nitric acid on *p*-iodoanisole is regarded as represented by the scheme



This is followed by the stages HOI + HI $\longrightarrow$ $I_2 + H_2O$; and



In the author's opinion, however, the preceding is not the course of the chief process giving rise to the iodonitroanisole, the formation of the major proportion of the iodonitroanisole resulting from the changes



(compare Robertson and Briscoe, T., 1912, **107**, 1965; Auwers and Dallwig, A., 1902, i, 218). D. F. T.

Polymerides of Anethole and *iso*Safrole. E. Puxeddu and L. Scaffidi (*Gazzetta*, 1916, **46**, ii, 169—176. Compare A., 1913, i, 460).—Anisoin has been prepared by (1) the action of sulphuric acid on anethole, (2) Orndorff, Terrasse, and Morton's method (A., 1898, i, 129), and (3) the action of sublimed ferric chloride on an ethereal solution of anethole. All these methods yield a white, mostly amorphous, but sometimes crystalline substance which, after purification, has m. p. 205—210°. The first method gives, in addition, a pale yellow, crystalline powder, m. p. about 250°, which is insoluble in ether and is apparently a polymeride of anethole; this compound also seems to be formed by the second method. Method (3) gives, besides anisoin, the polymeride already described (*loc. cit.*); the distillation products of this polymeride are being examined.

The action of bromine on an ethereal solution of anisoin (prepared by the action of sulphuric acid on anethole and carefully purified) cooled by means of an ice–salt mixture yields a compound which turns brown at 200°, becomes viscous at 230°, and then melts gradually, and contains 24·03—26·12% Br, which corresponds with a mixture of the compounds $C_{20}H_{22}O_2Br_2$ and $C_{20}H_{23}O_2Br$. Under similar conditions, the anisoin obtained by method (3) gives

a bromo-derivative containing a considerably lower proportion of bromine.

Cryoscopic measurements in benzene solution of the polymeride of *iso*safrole, obtained by treating an ethereal solution of the latter with ferric chloride and dry hydrogen chloride (*loc. cit.*), indicate that this polymeride is a dimeride. T. H. P.

Constitution and Stereochemical Isomerism of Polymerides of Phenols with Propenylic Side-chains. E. PUXEDDU and E. MARICA (*Gazzetta*, 1916, **46**, ii, 177—186).—The constitution of the polymerides of compounds such as *iso*eugenol, anethole, and *iso*safrole is discussed. These polymerides do not give the reactions characteristic of double linkings, and a diphenylic structure is not in accord with their chemical behaviour. The most probable hypothesis is that, like the truxillic acids (compare Liebermann, A., 1890, 1424; Liebermann and Sachs, A., 1893, i, 418), the polymerides possess a tetramethylenic configuration. The two principal possible structures have the forms $CHX<{CHX-\atop CHMe}>CHMe$ and $CHX<{CHMe\atop CHMe}>CHX$, where X represents the aromatic radicle. From the former, which contains four asymmetric carbon atoms and lacks any plane of symmetry, six isomerides are derivable, four of them being pairs of mirror images; from the second, which contains no asymmetric carbon atoms and possesses two planes of symmetry, five isomerides may be derived. Similar tetramethylenic constitution and stereoisomeric relations should hold also for all other polymerides arising from the fusion of two unsaturated chains. T. H. P.

2 : 6-Dinitroquinol. M. M. RICHTER (*Ber.*, 1916, **49**, 1398—1401).—The dinitroquinol which is obtained by nitrating quinol diacetate and then saponifying was presumed by Nietzki (1890) to be the 2:6-dinitro-derivative. A proof of this is now offered. Of the three possible dinitroquinols, it is the only one which could give two different mixed acetate–benzoates, and these have been isolated. If quinol monobenzoate is nitrated and then acetylated, a different product is obtained from that which results when dinitroquinol monoacetate is benzoylated.

Quinol monobenzoate is converted by nitration with fuming nitric acid in cold acetic acid into 2:6-*dinitroquinol* 4-*benzoate* (2 : 6-*dinitro*-4-*benzoyloxyphenol*), which crystallises in very slender, yellow needles, m. p. 151—152°, and forms red or orange alkali salts. On benzoylation, it yields 2 : 6-*dinitro*-1 : 4-*dibenzoyloxybenzene*, refractive, slender needles, m. p. 152—153°, and on acetylation it gives 2 : 6-*dinitro*-4-*benzoyloxy*-1-*acetoxybenzene*, pale yellowish-green, thin, rectangular leaflets, m. p. 153°. The isomeric 2 : 6-dinitro-1-benzoyloxy-4-acetoxybenzene has m. p. 128—129° (A., 1913, i, 1324).

If quinol monobenzoate is nitrated by dilute nitric acid in alcohol, it forms 2-*nitro*-4-*benzoyloxyphenol*, in golden-yellow,

woolly needles, m. p. 95—96°. This may be hydrolysed to form 2-nitroquinol, or further benzoylated to give the dibenzoate (Elbs, 1893).

Quinol monobenzoate may also be converted by acetylation into 4-*benzoyloxy*-1-*acetoxybenzene*, m. p. 122°. J. C. W.

2:3-Dihydroxytoluene (*iso*Homocatechol) and the Nitro-derivatives of its Methyl Ethers. RIKO MAJIMA and YOSHITARO OKAZAKI (*Ber.*, 1916, **49**, 1482—1496, and *Sci. Rep. Tôhoku Imp. Univ.*, 1916, **5**, 215—232).—2:3-Dihydroxytoluene is the lowest homologue of hydrourushiol (3-pentadecylcatechol), and therefore its properties and the nitro-derivatives of its dimethyl ether have been studied for comparison with those of the natural substance. The constitutions of the nitro-compounds have been determined independently and in ignorance of the methods adopted by Cain and Simonsen (T., 1914, **105**, 156) for the same purpose. The undoubted 5:6-dinitro-2:3-dimethoxytoluene which the authors have obtained differs from that of Cain and Simonsen, and the latter must be the alternative 4:6-compound, and its reduction product is therefore the 6-nitro-4-amino-compound (2-nitro-5:6-dimethoxy-*p*-toluidine). By the mild nitration of 3-hydroxy-*o*-tolyl methyl ether, both the 4- and 6-nitro-compounds have been obtained, the former being volatile in steam. The dimethyl ether of this, on oxidation, yields the 4-nitro-2:3-dimethoxybenzoic acid which Cain and Simonsen desired to isolate.

3-Hydroxy-*o*-tolyl methyl ether has b. p. 208—209°, and the solid with m. p. 39°, described as the pure substance, is really a hydrate with $\frac{1}{2}H_2O$. The isomeric 2-*hydroxy*-m-*tolyl methyl ether*, white prisms, m. p. 41—42°, is obtained by the reduction of *o*-vanillin by Clemmensen's method. Both ethers yield 2:3-dihydroxytoluene on hydrolysis with hydrobromic acid in a sealed tube at 150°, and this has b. p. 134—136°/15 mm., m. p. 45°, and resembles hydrourushiol in various colour reactions. They also yield 2:3-dimethoxytoluene on methylation. This forms 5-nitro-2:3-dimethoxytoluene on treatment with nitric acid (D 1·4) and glacial acetic acid (the m. p. is 75—76°, and not 175—176° as given by Cain and Simonsen), and also 3-methoxy-*o*-toluquinone, m. p. 147—149°, which remains in the acid mother liquor. The quinol corresponding with this has m. p. 124—127° (compare Henrich and Nachtigall, A., 1903, i, 414), whilst 6-*methoxy*-o-*toluquinol*, obtained from 2-methoxy-*m*-toluidine, forms white needles, m. p. 117—118°. The 5-nitro-compound yields 5:6-*dimethoxy*-m-*toluidine* on reduction, in colourless crystals, m. p. 62—63° (hydrochloride, m. p. 200°), and this gives 5:6-*dimethoxy*-m-*cresol*, monoclinic plates, m. p. 140—141°, after diazotisation. Both amine and phenol yield the above quinone, m. p. 147—148°, on oxidation.

2:3:4-Trihydroxybenzaldehyde yields 2:3:4-*trihydroxytoluene*, white needles, m. p. 140—141°, on reduction with amalgamated zinc and hydrochloric acid, and the corresponding trimethoxytoluene forms solid nitro-compounds.

5 : 6-*Dinitro*-2 : 3-*dimethoxytoluene* is obtained from the 5-nitro-compound by means of fuming nitric acid. It forms long prisms, m. p. 105—106°, and yields 2-*nitro*-5 : 6-*dimethoxy*-m-*toluidine* on reduction with alcoholic ammonium sulphide, in orange-coloured crystals, m. p. 112—113°. The amine is converted into 6-nitro-2 : 3-dimethoxytoluene on treatment with amyl nitrite and alcohol (Cain and Simonsen).

3-Hydroxy-*o*-tolyl methyl ether, when nitrated at below −10°, yields 4-*nitro*-3-*hydroxy*-o-*tolyl methyl ether*, yellow needles, m. p. 59—60°, volatile in steam, and the 6-*nitro*-compound, white crystals, m. p. 91—92°, mixed with a little of 4 : 6-*dinitro*-3-*hydroxy*-o-*tolyl methyl ether* (Cain and Simonsen's 5 : 6-dinitro-compound). The first-named forms 4-*nitro*-2 : 3-*dimethoxytoluene* on methylation, and this gives 4-*nitro*-2 : 3-*dimethoxybenzoic acid*, pale yellow needles, m. p. 94—95°, on oxidation with alkaline permanganate, and 4 : 5-*dinitro*-2 : 3-*dimethoxytoluene*, m. p. 126—127°, on treatment with fuming nitric and acetic acids. Finally, either the 4 : 5- or 4 : 6-dinitro-compound yields 4 : 5 : 6-*trinitro*-2 : 3-*dimethoxytoluene*, white needles, m. p. 131—132°, on boiling with fuming nitric acid.

All the nitro-compounds of 2 : 3-dimethoxytoluene are therefore now well established. Their m. p.'s are summarised below:

Position of the NO_2 groups	4	5	6	4 : 5	5 : 6	4 : 6	4 : 5 : 6
M.p.......	liquid	75—76°	45—46°	126—127°	105—106°	76—77°	131—132°

J. C. W.

Preparation of Halogen-substituted Tellurium Compounds. KARL LEDERER (*Ber.*, 1916, **49**, 2002—2005).—Diphenylsulphonium dibromide, SPh_2Br_2, changes readily at the ordinary temperature into mono- and di-bromodiphenyl sulphides; diphenylselenonium dichloride also changes into dichlorodiphenyl selenide on heating. The corresponding telluronium salts, however, are stable, but dihalogenodiaryl tellurides may be prepared by the action of tellurium dibromide on magnesium halogenoaryl haloids.

Thus, magnesium *p*-chlorophenyl bromide and tellurium dibromide yield di-*p*-chlorodiphenyl telluride, which combines with bromine to form *di*-p-*chlorodiphenyltelluronium dibromide*, $TeBr_2(C_6H_4Cl)_2$, a yellow, crystalline powder with m. p. 184—185°. Similarly, magnesium *p*-bromophenyl bromide yields *di*-p-*bromodiphenyltelluronium dibromide*, a yellow, crystalline powder, m. p. 195—196°, and also a little of p-*bromophenyl*-p′-*bromodiphenylyltelluronium dibromide*, $TeBr_2(C_6H_4Br)(C_6H_4 \cdot C_6H_4Br)$, which is an insoluble powder. J. C. W.

Attempts to Prepare Optically Active Tellurium Compounds. Phenyl-*p*-tolyltellurium Compounds. KARL LEDERER (*Ber.*, 1916, **49**, 1615—1622).—Triaryltelluronium haloids are conveniently prepared by the action of Grignard agents on diaryltelluronium

dihaloids, thus: $TeR_2X_2 + MgR'X = TeR_2R'X + MgX_2$; and mixed triaryltelluronium haloids can be reduced by treatment with a further quantity of an organomagnesium salt to mixed diaryl tellurides, thus: $TeR_2R'X + MgR'X = TeRR' + RR' + MgX_2$.

For example, di-*p*-tolyltelluronium dichloride and magnesium phenyl bromide (1 mol.) yield a compound which is precipitated by the addition of potassium iodide as *phenyldi*-p-*tolyltelluronium iodide.* This crystallises in tetragonal columns, m. p. 209—210°, whilst the corresponding *bromide* forms small nodules, m. p. 230—231°, and the *picrate* rosettes of yellow, rhombic platelets, m. p. 132—133°. For the preparation of the phenyl tolyl telluride, the ditolyltelluronium dichloride may be treated directly with an excess (5 mols.) of magnesium phenyl bromide, and the crude dibromide which separates deprived of bromine by means of sodium hydrogen sulphite. *Phenyl* p-*tolyl telluride*, $TePh{\cdot}C_7H_7$, crystallises in slender needles, m. p. 63—64°, b. p. 207—208°/16 mm., and yields the following *phenyl*-p-*tolyltelluronium* compounds: *dichloride*, needles, m. p. 135—136°; *dibromide*, m. p. 175—176°; *di-iodide*, reddish-brown columns, m. p. 195°, or carmine-red needles, m. p. 204°; *oxide*, white granules; *anhydride* of the *basic chloride*, $(TeRR'Cl)_2O$, microscopic columns, m. p. 243—244°; *anhydride* of the *basic bromide*, m. p. 259—260°; *basic iodide*, $TeRR'I{\cdot}OH$, a yellow, amorphous powder, m. p. 200—201°. The telluride also reacts with methyl iodide to form *phenyl*-p-*tolylmethyltelluronium iodide*, m. p. 73—74°, and yields *double* salts with the mercuric haloids (*chloride*, $TeRR',HgCl_2$, a white powder, m. p. 91°; *bromide*, m. p. 54°; *iodide*, m. p. 74°). J. C. W.

Action of Grignard Solutions on Tellurium Tetrachloride. KARL LEDERER (*Ber.*, 1916, **49**, 1385—1389).—Triphenyl- and tritolyl-telluronium salts were prepared by the author in 1911 by the action of the magnesium aryl haloids on tellurium tetrachloride. Similar salts are described in this paper.

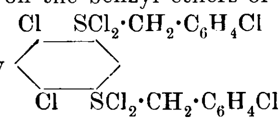
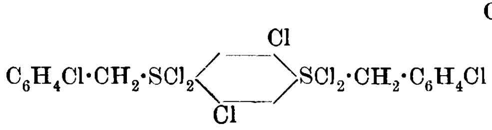
The *tri*-m-*tolyltelluronium* salts, $TeX(C_7H_7)_3$, are as follows: *iodide*, scales, m. p. 160—161°; *picrate*, small needles, m. p. 152—153°; *double salt* with mercuric chloride, $TeCl(C_7H_7)_3,HgCl_2$, white leaflets, m. p. 159—160°. *Tri*-p-*xylyl*-5-*telluronium iodide* forms elongated, four-sided leaflets, m. p. 186—187°; *tri*-m-*xylyl*-4-*telluronium iodide* crystallises in colourless needles, m. p. 208—209°, and the *picrate* has m. p. 138—139°. *Tri*-p-*anisyltelluronium iodide* is a crystalline powder, m. p. 160°, and the *picrate* forms rhombic tablets, m. p. 160°. *Trimesityltelluronium iodide* crystallises in small, white needles, m. p. 169—170°, and the *bromide* has m. p. 164°. J. C. W.

Basic Properties of the Sulphoxides. CESARE FINZI (*Gazzetta*, 1916, **46**, ii, 186—203).—The author's investigations were made with the view of ascertaining if, and in what degree, basic properties are exhibited by the sulphoxides of ethers obtained from thioresorcinol and thioquinol, in order to establish the influence exerted by the nature of the etherifying group and by the relative positions of the two sulphur atoms in the nucleus.

The results obtained by Zincke and his collaborators (A., 1909, i, 643; 1913, i, 44) and by the author and his co-workers (A., 1914, i, 294, 1130, 1132), together with those now described, lead to the following general considerations.

When treated with bromine, ethers of thioresorcinol always give, as initial products, derivatives of nuclear substitution, even when anhydrous solvents and low temperatures are employed. None gives products of salification with the exception of the ethyl ether, in which case the two sulphur atoms may, after the nuclear substitution, combine in a labile manner with four atoms of bromine. On the other hand, the ethers of thioquinol, with the exception of the acetyl derivative, yield products of salt formation when treated with bromine. The author has prepared *p*-diphenacylthiolbenzene, and finds that this compound, under suitable conditions of temperature, yields a tetrabromide. Removal of the latter from the freezing mixture in which it is formed results in loss of hydrogen bromide, bromine migrating from the sulphur to the nuclear carbon atoms giving 2 : 5-dibromo-*p*-diphenacylthiolbenzene. The latter may also be obtained directly by the action of bromine on *p*-diphenacylthiolbenzene at the ordinary temperature. Further action of bromine on this 2 : 5-dibromo-compound results in the introduction of two other bromine atoms, probably in the aromatic nuclei of the phenacyl radicles.

The action of iodine gives substitution products with neither of the two thiophenols, and only for the methyl and benzyl ethers of thioquinol are additive products obtained; these periodides are far more stable than the corresponding perbromides.

The action of chlorine in anhydrous solvents results always in decomposition, which, with the phenylenedithiolacetic acids, takes place in accordance with the equation $C_6H_4(S{\cdot}CH_2{\cdot}CO_2H)_2 + 6Cl_2 = 6HCl + 2CO_2 + C_6H_4(S{\cdot}CCl_3)_2$. Under similar conditions, dibenzylthioresorcinol yields 4 : 6-dichloro-1 : 3-dichlorothiolbenzene (compare Zincke, A., 1911, i, 368) and dibenzylthioquinol gives an apparently analogous compound, but this was obtained in such small amount that the analytical data are uncertain. The results obtained when chlorine acts on the solid ethers in absence of solvent point to the formation at low temperatures of chlorides which are extremely unstable, and decompose, with swelling and evolution of chlorine, immediately they are removed from the freezing mixture. In one case, the sulphoxide was separated, its formation being explainable only by the reaction $C_6H_4(SCl_2{\cdot}CH_2Ph)_2 + 2H_2O = 4HCl + C_6H_4(SO{\cdot}CH_2Ph)_2$. The original products formed by the action of chlorine at low temperatures on the benzyl ethers of thioresorcinol and thioquinol are probably  and ; at the ordinary tem-

perature the former of these decomposes, yielding 4:6-dichloro-1:3-dichlorothiolbenzene (see above).

The action of hydrogen chloride on the solid sulphoxide of dibenzylthioresorcinol in the cold results in the addition of 2HCl and formation of the oily *compound*, $C_6H_4[SCl(OH)\cdot CH_2Ph]_2$, which is highly unstable. In the case of the sulphoxide of dibenzylquinol, quantitative addition of hydrogen chloride does not occur, the substance decomposing.

The conclusion is drawn that thioresorcinol and thioquinol are feebly basic in character, this being more apparent in derivatives of the former than in those of the latter. The more negative the etherifying groups, the more difficult is the detection of the basicity.

p-*Diphenacylthiolbenzene*, $C_6H_4(S\cdot CH_2\cdot COPh)_2$, obtained by the condensation of thioquinol with phenacyl bromide, forms slender, white laminæ, m. p. 146°, and its *dioxime*, $C_{22}H_{20}O_2N_2S_2$, small, white needles, m. p. 174°.

p-*Diphenacylsulphonylbenzene*, $C_6H_4(SO_2\cdot CH_2\cdot COPh)_2$, prepared by oxidising *p*-diphenacylthiolbenzene with permanganate, forms long plates, m. p. 195°.

p-*Diphenacylthiolbenzene tetrabromide*, $C_6H_4(SBr_2\cdot CH_2\cdot COPh)_2$, is an unstable, red, crystalline compound.

2:5-*Dibromo*-p-*diphenacylthiolbenzene*, $C_6H_2Br_2(S\cdot CH_2\cdot COPh)_2$, forms pointed, crystalline masses softening at 110°, m. p. 112°.

2:5-*Dibromodi*-p-*bromophenacylthiolbenzene* (?),

$$C_6H_2Br_2(S\cdot CH_2\cdot CO\cdot C_6H_4Br)_2,$$

forms small, yellow prisms, m. p. 201° (frothing). T. H. P.

αα-Diarylglycerols. C. PAAL [with KURT ZAHN and MAX KINSCHER] (*Ber.*, 1916, **49**, 1567—1583).—Some reactions of αα-diphenylglycerol (A., 1907, i, 522) are described. A complicated mixture of intra- and inter-molecular anhydrides is obtained on heating the compound with dilute sulphuric acid, and many experiments have been made with the aim of identifying some of these.

αα-Diphenylglycerol forms a βγ-*diacetate*,

$$OH\cdot CPh_2\cdot CH(OAc)\cdot CH_2\cdot OAc,$$

elongated leaflets, m. p. 129—131°, and a βγ-*dibenzoate*, nodules of slender needles, m. p. 180°, when treated with the acyl chlorides and pyridine.

On oxidation with permanganate in aqueous acetone, the compound yields benzophenone and glycollic acid, identified as the phenylhydrazone and lead salt respectively.

The mixture of anhydrides consists of an oily, crystalline mass. The oil may be removed by washing with cold alcohol. The crystalline portion has yielded the following substances: a *compound*, $C_{30}H_{26}O_3$ ($2C_{15}H_{16}O_3-3H_2O$), m. p. 135—136°; an *oxime*, $C_{15}H_{12}\!:\!N\cdot OH$, small tablets, m. p. 109—111°; a *semicarbazone*, $C_{15}H_{14}O\!:\!N\cdot NH\cdot CO\cdot NH_2$, prisms, m. p. 207—208° (decomp.); a mixture of semicarbazones of a dianhydro-compound; on oxidation, a mixture of acids and benzophenone. The liquid portion (80% of the whole) has given the following: the above oxime, m. p.

109—110°; another *oxime*, silky needles, m. p. 141—143°, probably an aldoxime; the above semicarbazones; on oxidation, much benzophenone and acids not identical with those derived from the solid portion.

The anhydride mixture was also distilled, and a fraction, b. p. 176—178°/20 mm., 53% of the whole, was found to contain aldehydes. The only individual compound which has been isolated so far is the *compound* $C_{15}H_{14}O_2$, slender needles, m. p. 181—183°. The oily part of the mixture was also distilled separately, and the fraction, b. p. 200—205°/30 mm., was treated with sodium hydrogen sulphite and other appropriate agents, when a non-aldehydic, cyclic compound, m. p. 169—171°, was isolated.

r-*αα-Di*-p-*tolylglycerol*, needles, m. p. 116—117°, and r-*αα-dibenzylglycerol*, needles, m. p. 93—94°, are prepared by the action of an excess of magnesium *p*-tolyl bromide and magnesium benzyl chloride respectively on methyl *r*-glycerate. J. C. W.

Cholesterol. XXIV. Transformation of Cholesterol into Coprosterol. A. WINDAUS (*Ber.*, 1916, **49**, 1724—1734).—The knowledge of the reduction products of cholesterol gained in recent years has now enabled the author to achieve his main purpose, the artificial production of that alcohol which is obtained by the reductive action of intestinal bacteria, namely, coprosterol. It is still impossible to say why so many different dihydrocholesterols are formed when different reducing agents are employed.

Cholesterol is reduced by means of hydrogen at 200° in the presence of nickel (made by reducing the voluminous oxide obtained on dropping a concentrated solution of the nitrate and dextrose into a red-hot crucible) with the formation of *γ-cholestanol*, which crystallises in large tablets, m. p. 146°, $[\alpha]_D^{18}$ +29·9°. This is really a conglomeration of *β*-, *δ*-, and *ε*-cholestanols in the sense of the partial racemate compounded of *β*-cholestanol and *ψ*-coprosterol (A., 1915, i, 679), and it was the failure to recognise this fact which has delayed the research until now. The *β*-cholestanol can be removed by precipitation with digitonin, and the isomerides which do not combine with this glucoside may be partly separated by crystallisation from methyl alcohol. *ε*-Cholestanol separates first, and the part which remains in the crude *δ*-cholestanol is rearranged into *β*-cholestanol by boiling the mixture with sodium and xylene. This *β*-cholestanol is again precipitated with digitonin, and the pure *δ*-cholestanol is obtained in long, slender needles, m. p. 116—118°, $[\alpha]_D^{18}$ +31·62°. This is shown to be identical with the *ψ*-coprosterol derived from coprosterol by converting both into (1) the acetate, (2) *δ*-cholestane (coprostane or *ψ*-cholestane), (3) a *ketone*, $C_{27}H_{46}O$, m. p. 61—62°, and (4) an acid, $C_{27}H_{46}O_4$, which forms a *methyl* ester, long, thin needles, m. p. 61° (compare Dorée and Gardner, T., 1908, **93**, 1328, 1625; Mauthner, A., 1909, i, 714; Gardner and Godden, A., 1914, i, 169; and Adamla, *Diss.*, Freiburg, 1911). Finally, the *δ*-cholestanol is partly transformed into the isomeric coprosterol by heating with

alcoholic sodium ethoxide at 180°. The coprosterol is precipitated by digitonin from the mixture and recovered by extracting the double compound with boiling xylene. The "synthetic" coprosterol crystallises in long, stout needles, m. p. 101—102°, $[\alpha]_D^{21}$ +23·55°, and forms a characteristic propionate, in long needles, m. p. 99—100°. J. C. W.

Naphthenic Acids. G. von Kozicki and St. von Pilat (*Chem. Zentr.*, 1916, i, 1145—1146; from *Petroleum*, 1916, **11**, 310—316). —By conversion of the naphthenic acids successively into the acid chlorides, nitriles, amides, and amino-bases, the authors show that the naphthenic acids of Galician petroleum distillates are carboxylic acids which contain one carboxyl group and agree in their properties with the naphthenic acids of Russian petroleum. The acids are readily esterified in light petroleum solution. The proportion of naphthenic acids in the distillates increases on long keeping, especially under the influence of light and atmospheric oxygen.

The properties of the various acids separated and of their derivatives are as follows:

Formulæ.	D. of methyl ester.	B. p. of methyl ester.	B. p. of acid chloride.	B. p. of free acid.
$C_7H_{13}\cdot CO_2H$	0·9105	185—193°	192—196° (191·5—196·5)	236—238
$C_8H_{15}\cdot CO_2H$	0·9320	210—214	206—212	250—253
$C_9H_{17}\cdot CO_2H$	0·935	219—225	227—230	260—264
$C_{10}H_{19}\cdot CO_2H$	0·923	205—210	215—219	255—258
$C_{11}H_{21}\cdot CO_2H$	0·933	226—230	228—234	268—272
$C_{12}H_{23}\cdot CO_2H$	0·9275	235—240	238—241·5	272—275
$C_{13}H_{25}\cdot CO_2H$	0·9175	258—263	247—251	283—287
$C_{14}H_{27}\cdot CO_2H$	0·937	280—290	283—287	300—303

Methyl dodecanaphthenecarboxylate, $C_{12}H_{23}\cdot CO_2Me$, is a pale yellow liquid with a pleasant odour, b. p. 237—239°, $D^{20\cdot 5}$ 0·9275. The following derivatives of the acid have been prepared: *calcium* salt, yellow powder; *manganese* salt, yellow powder; *cobalt* salt, pale violet, crystalline powder, converted by ammonia into the pale green *ammino*-salt, $Co(NH_3)_4(CO_2\cdot C_{12}H_{23})_2$; *magnesium* salt, white powder; *dinitrophenyl* ester, $C_{12}H_{23}\cdot CO_2\cdot C_6H_3(NO_2)_2$, brown, acicular crystals, exploding at 110°; *amide*, $C_{13}H_{25}ON$, colourless needles, m. p. 138°, subliming below 100°; *nitrile*, $C_{12}H_{23}\cdot CN$, yellow liquid of characteristic odour, b. p. 250—252°, turning dark in the light, but not affected by hydrogen peroxide; *amine*, $C_{12}H_{23}\cdot CH_2\cdot NH_2$, pale yellow, viscous liquid, which fumes in presence of hydrogen chloride and extracts carbon dioxide from the air with formation of a gelatinous mass; *acetylamino*-derivative, $C_{12}H_{23}\cdot CH_2\cdot NHAc$, reddish-yellow, viscous oil; *oxalate* of the amine, m. p. 162° (corr.). Treatment of the amine with nitrous acid results in liberation of nitrogen and formation of a reddish-yellow oil, b. p. 217° (decomp.), which is apparently the corresponding alcohol. T. H. P.

Preparation of Nitriles. AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P., 293094; from *J. Soc. Chem. Ind.*, 1916, **35**, 1055).—Nitriles may be prepared by heating aromatic compounds containing halogen combined directly with the nucleus with finely divided or dissolved, simple or complex metallic cyanogen compounds, with the addition of a substance which promotes the change at temperatures up to 350°. Compounds in which the halogen atom is rendered mobile by the presence of a nitro-group in the ortho- or para-position are unsuitable, and the action of cuprous cyanide on halogenanthraquinones is disclaimed. The following examples are cited: (1) finely ground anhydrous calcium ferrocyanide (14 parts), Fuller's earth (6 parts), copper powder (1 part), and chlorobenzene (44 parts) are heated at 300—320° for twenty hours; α-chloronaphthalene (18 parts), pyridine (60 parts), and copper ferrocyanide (8 parts) are heated at 270° for eighteen hours.

H. W.

Some Derivatives of Isethionic Acid. E. SALKOWSKI (*Ber* 1916, **49**, 1376—1382).—Among other attempts to prepare more soluble, but physiologically active derivatives of the anæsthetic, ethyl *p*-aminobenzoate, the author has heated the ester with technical 50% isethionic acid, first evaporating the solution to dryness and then keeping the residue at 140—150° for a few hours. In this way, p-*isethionylaminobenzoic acid* (p-β-*hydroxyethanesulphonylaminobenzoic acid*), $CO_2H\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_2H_4\cdot OH$, is obtained as an almost colourless, silky mass, which is sparingly soluble in hot water, acid to Congo-red, and not molten at 260° (*silver* salt; *sodium* salt, very long, thin, hexagonal leaflets). The potassium salt is quite without anæsthetic properties.

The same acid is formed directly from free *p*-aminobenzoic acid, and similar compounds are given by the isomerides; o-*isethionylaminobenzoic acid* has m. p. 262° (decomp.) and m-*isethionylaminobenzoic acid* has m. p. 252° (decomp.). Other amino-acids and substituted benzoic acids also react with isethionic acid.

The silver salt of the above acid reacts very quickly with ethyl iodide in the cold, but only traces of an ester are formed, mixed with the free acid.

J. C. W.

Salts of *o*- and *p*-Nitrophenylacetic Esters. ST. OPOLSKI and T. ZWISLOCKI (*Ber.*, 1916, **49**, 1606—1607).—Salts of the type $CO_2Et\cdot CH\colon C_6H_4\colon NO\cdot OM$ have been obtained as precipitates by adding alkali ethoxides to ethereal solutions of ethyl *o*- and *p*-nitrophenylacetates. The *sodium* and *potassium* salts are dark violet in the case of the ortho-compound and dark brown in the case of the para-ester.

J. C. W.

Experiments on the Walden Inversion. IV. The Influence of the Solvent on the Sign of the Product in the Conversion of Phenylchloroacetic Acid to Phenylaminoacetic Acid. GEORGE SENTER and HARRY DUGALD KEITH DREW (T., 1916, **109**, 1091—1106).—In a previous paper (T., 1915, **107**, 638) it was

shown that the displacement of chlorine in ammonium phenylchloroacetate by the amino-group gives rise to a product of the opposite sign when the reaction takes place in aqueous solution, whilst the reaction in acetonitrile yields a product of the same sign.

Further experiments made with twelve different solvents show that in six cases change of sign occurs, whilst in the remaining six the resulting amino-acid has the same sign as the original chloro-acid.

When water and liquid ammonia are used as solvents, relatively very active products of opposite sign are obtained, and on this account the reaction in these solvents has been more closely investigated. In aqueous solution, the concentration of the chloro-acid has but little influence on the activity of the product, but racemisation increases with rise of temperature. In liquid ammonia, on the other hand, the activity of the product decreases with increase in the concentration of the chloro-acid, although the temperature has little influence on the result. The increase in the racemisation in concentrated solutions in liquid ammonia has been traced to the action of ammonium chloride. Ammonium and sodium nitrate show a similar effect.

From certain solutions, in particular from liquid ammonia, a further active product was isolated, which has been found to consist of partly racemised iminodiphenyldiacetic acid, $NH(CHPh{\cdot}CO_2H)_2$.

It is considered that a satisfactory explanation of the Walden inversion is not likely to be attained on the basis of the theories put forward by Fischer and by Werner. Although no other explanation has yet been found, it is suggested that the products of opposite sign may possibly be due to the reaction between ammonia and the phenylchloroacetate molecule and ion respectively, or to the action of free and combined ammonia on the phenylchloroacetate. The predominant reaction would then depend on the nature of the solvent. H. M. D.

Naphthylacetic Acids. I. FRITZ MAYER and TRUDI OPPENHEIMER (*Ber.*, 1916, **49**, 2137—2141).—α- and β-Naphthylacetic acids can be obtained in satisfactory quantities from the technical methylnaphthalenes by brominating these, converting the bromides into the nitriles by means of sodium cyanide, and hydrolysing these by treatment with potassium hydroxide and hydrogen peroxide.

4-Nitro-1-methylnaphthalene reacts with ethyl oxalate in the presence of sodium ethoxide to form 4:4′-*dinitrodi*-1-*naphthylethane*, $C_2H_4(C_{10}H_6{\cdot}NO_2)_2$, which crystallises in brownish-yellow needles, m. p. 257°, but 1-nitro-2-methylnaphthalene behaves in the normal way (compare Reissert, A., 1897, i, 417), yielding 1-*nitro*-2-*naphthylpyruvic acid*, $NO_2{\cdot}C_{10}H_6{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$, in sulphur-yellow crystals, m. p. 206°. This forms a *methyl* ester, in brownish-yellow crystals, m. p. 130°, and is oxidised by alkaline hydrogen peroxide to 1-*nitro*-2-*naphthylacetic acid*,

$$NO_2{\cdot}C_{10}H_6{\cdot}CH_2{\cdot}CO_2H,$$

which separates in pale yellow crystals, m. p. 206—207°, and yields a grey *methyl* ester, m. p. 94—95°. J. C. W.

Semicarbazones of α-Ketonic Acids. α-Iodocinnamic Acids. J. BOUGAULT (*Compt. rend.*, 1916, **163**, 363—366).—By the addition of iodine to an alkaline solution of the semicarbazone of an α-ketonic acid, the semicarbazide group is removed and a di-iodo-acid is formed which often at once passes into an unsaturated α-iodo-acid. In this way, phenylpyruvic acid semicarbazone is readily converted into a mixture of the stereoisomeric *α-iodocinnamic acids*, $CHPh:CI\cdot CO_2H$. These two acids can be easily separated by conversion into their potassium salts, that of the stable form being insoluble and that of the labile form soluble. The stable form has m. p. 160—162°, the labile form m. p. 108—110°, and the labile form is converted into the stable form by heating it for a few hours with pyridine on a water-bath. The two acids, in solution, readily oxidise in the air with the liberation of iodine. When reduced with zinc and acetic acid, they give ordinary cinnamic acid, and when heated on a water-bath with aqueous sodium carbonate they are slowly converted into phenylpyruvic acid. They both give *acid potassium* salts,

$$(CHPh:CI\cdot CO_2)_2KH.$$

The author has prepared the β-iodocinnamic acid, m. p. 160—162°, described by Ortoleva (compare A., 1899, i, 894), and finds it to be identical with his stable α-iodocinnamic acid. W. G.

Deduction of Valency Laws. Principle of Variable States [Conditioning Formulæ]. HUGO KAUFFMANN (*Ber.*, 1916, **49** 1324—1337. Compare A., 1909, ii, 107).—Some additional evidence is given to show that the variations in colour which some fluorescent substances suffer in different solvents may not necessarily be due to dynamic or geometric isomerism or polymerism. The idea that the molecule undergoes changes in internal state other than actual alteration in constitution is developed further, and examples of the derivation of "conditioning formulæ" or "formulæ of state," involving the divisibility of valencies, are given. The principle is laid down that the extent of the saturation of the valencies is not to be represented in these formulæ by invariable numerical values, but that reactive parts of the molecule shall be characterised by large deviations and indifferent parts by small deviations from these values. In the light of these conceptions, the chemical activity of methyl iodide can only be explained by assuming that the iodine atom is more than univalent.

In order to preclude the possibility of ortho- or para-quinone isomerism, search was made for a meta-derivative which exhibited the variable fluorescence. Such a compound is *ethyl* m-*amino-α-cyanocinnamate*, $NH_2\cdot C_6H_4\cdot CH:C(CN)\cdot CO_2Et$,, which is obtained by reducing the nitro-compound, the product of the condensation of *m*-nitrobenzaldehyde with ethyl cyanoacetate, with alcoholic stannous chloride. It forms orange crystals, m. p. 102°, and exhibits a blue fluorescence in light petroleum, a yellowish-green in ether, a greenish-blue in carbon tetrachloride and carbon

disulphide, and a green in benzene. The *acetyl* derivative is a pale yellow, granular substance, m. p. 143°, and the free *acid*, obtained by hydrolysis with dilute sulphuric acid, is almost white and has m. p. 207° (decomp.). Striking fluorescence, varying from violet to green, is also exhibited by *m-amino-ω-cyanostilbene*, $NH_2 \cdot C_6H_4 \cdot CH:CPh \cdot CN$, which is obtained in small, yellow crystals, m. p. 127°, by reducing the product of the condensation of *m*-nitrobenzaldehyde with phenylacetonitrile. The *acetyl* derivative has m. p. 138°, the *benzoyl* m. p. 156°; the *benzenesulphonyl* compound is white and has m. p. 123°, and the *methyl ether* of this, $SO_2Ph \cdot NMe \cdot C_6H_4 \cdot CH:CPh \cdot CN$, has m. p. 105°. When the base is warmed with methyl sulphate in the presence of magnesia, it forms the white quaternary *ammonium* salt,

$$OMe \cdot SO_2 \cdot O \cdot NMe_3 \cdot C_6H_4 \cdot CH:CPh \cdot CN,$$

m. p. 172°, which is transformed by potassium iodide into the methiodide, m. p. 159—162° (decomp.).

2:5-Dimethoxybenzaldehyde, prepared by Gattermann's method, condenses with ethyl cyanoacetate to form *ethyl α-cyano-*2:5-*dimethoxycinnamate*, which crystallises on quickly cooling an alcoholic solution as a mixture of orange-red and yellow varieties. These can be mechanically separated by working in the light of a mercury lamp shaded by a blue screen, for the yellow crystals then glow with a greenish-yellow light, whilst the others are almost invisible. The orange-red crystals have m. p. 85°, and the yellow ones begin to redden at 70° and are completely changed at 78° into the red modification. The yellow form can be isolated by allowing a cold alcoholic solution to evaporate slowly, but the tendency for solutions to become red is very great. Both forms exhibit fluorescence varying from violet to green, according to the solvent. The free *acid*, $C_6H_3(OMe)_2 \cdot CH:C(CN) \cdot CO_2H$, forms orange needles, m. p. 227°; alcoholic solutions are yellow and exhibit green fluorescence, whilst solutions of the sodium salt are colourless and exhibit blue fluorescence.

As a compound in which geometric isomerism is impossible to explain varying fluorescence, 2:5-*dimethoxybenzylidenemalononitrile*, $C_6H_3(OMe)_2 \cdot CH:C(CN)_2$, is described. This forms orange leaflets, m. p. 110°, and exhibits strong fluorescence varying from blue to yellowish-green.

*Phenyl cyano-*2:5-*dimethoxystyryl ketone*,

$$C_6H_3(OMe)_2 \cdot CH:CBz \cdot CN,$$

the product of the condensation of cyanoacetophenone with 2:5-dimethoxybenzaldehyde, also exists in two forms, orange-red, m. p. 130°, and yellow, m. p. 124° (changing into the red), which are mutually interchangeable, for it separates on crystallisation into sometimes one, sometimes the other form, apparently without reason. The colours of the solutions are identical in the two cases and exhibit the same varying fluorescence. J. C. W.

Some Ortho-derivatives of Cinnamic Acid. S. GABRIEL (*Ber.*, 1916, **49**, 1608—1613).—*o*-Nitrocinnamic acid is best prepared from *o*-nitrobenzaldehyde by Perkin's method.

o-*Phthalimidocinnamic acid*, $C_8H_4O_2{:}N{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$, is obtained in short prisms, m. p. 240—241°, by heating *o*-amino-cinnamic acid with phthalic anhydride at 210°. It may be converted through the chloride into the *amide*, rhombic plates, m. p. 258—260°, and this may be transformed into indole by the following means: it is first mixed with sodium hypochlorite and methyl alcohol, then the resulting ester,

$$C_8H_4O_2{:}N{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}NH{\cdot}CO_2Me,$$

is evaporated to dryness, warmed with hydrochloric acid, and the product distilled with potassium hydroxide (compare Weerman, A., 1913, i, 1195).

o-Cyanocinnamic acid is best obtained by diazotising *o*-amino-cinnamic acid and warming the solution with copper sulphate and potassium cyanide. The *chloride*, $CN{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COCl$, has m. p. 94—96°, and the *amide*, needles and leaflets, m. p. 203—204°, is converted by Weerman's method into *methyl* o-*cyanostyryl-carbamate*, $CN{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}NH{\cdot}CO_2Me$, m. p. 175°. This undergoes hydrolysis on boiling with 20% hydrochloric acid to *o*-cyano-phenylacetaldehyde, and then the *o*-amido-compound, and this straightway loses the elements of water and forms *iso*carbostyril, $C_6H_4{<}\begin{matrix}CH{:}CH\\ CO{-}NH\end{matrix}$.

o-Carboxycinnamic acid yields a *dichloride*,

$$COCl{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}COCl,$$

needles, m. p. 69·5—70·5°, and a *diamide*, long needles, m. p. 200—201°.

Phthalaldehydic acid (*o*-aldehydobenzoic acid) yields *α-chloro-phthalide*, $C_6H_4{<}\begin{matrix}CHCl\\ CO{-}{-}\end{matrix}{>}O$, m. p. 61°, when boiled with thionyl chloride, and this is also obtained by chlorinating phthalide at 140°. J. C. W.

Mercury Salicylate and *o*-Methoxybenzoate. L. Reutter (*Chem. Zentr.*, 1916, ii, 12; from *Schweiz. Apoth.-Zeit.*, 1916, **54**, 126).—The interaction of yellow mercuric oxide or mercuric acetate and *o*-methoxybenzoic acid in boiling aqueous solution yields the basic *mercury* salt, $OMe{\cdot}C_6H_3{<}\begin{matrix}CO\\ Hg\end{matrix}{>}O$, whilst sodium *o*-methoxybenzoate and a mercury salt give the normal *mercuric* o-*methoxybenzoate*, $(OMe{\cdot}C_6H_4{\cdot}CO_2)_2Hg$. T. H. P.

Aspirin. Solidification, in Concentric Rings, of Molten or Dissolved Aspirin. D. E. Tsakalotos and S. Horsch (*Bull. Soc. chim.*, 1916, [iv], **19**, 321—326).—Aspirin, when heated just to its melting point on a glass slide and allowed to cool, solidifies for the most part in concentric rings, forming round a circular centre, the rings widening from the centre outwards. A similar formation is often obtained from solutions in ethyl or methyl alcohol or acetone, except that the centre of the rings is usually occupied by a prismatic crystal. Aspirin also solidifies in dendritic forms, and all three forms have been observed combined in the crystallisation of

aspirin from its solution in acetone. In certain cases a helical formation was obtained instead of the rings. W. G.

Demethylation of Phenol Ethers and Esters by means of the Hydrochlorides of Aromatic Bases. Preparation of Anilides and their Homologues. ALFONS KLEMENC (*Ber.*, 1916, **49**, 1371—1376).—Many phenol ethers, or phenol ether carboxylic acids or their esters, can be demethylated, usually in less than an hour, by melting them with aniline or toluidine hydrochlorides, the acids or esters yielding anilides.

Thus, anisic acid yields *p*-hydroxybenzamide, m. p. 201—202°, p-*hydroxybenzo*-p-*toluidide*, long, hard needles, m. p. 207—209°, and p-*hydroxybenzo*-m-*toluidide*, small, white crystals. *m*-Methoxybenzoic acid forms *m*-hydroxybenzamide, m. p. 156°. Hemipinic acid first changes to the anhydride and then forms *norhemipinic anil* (3 : 4-*dihydroxyphthalanil*), $C_{14}H_9O_4N$, as a pale pink substance, m. p 226°.

Demethylation of an ether–acid without the formation of an anilide can sometimes be effected with dimethylaniline hydrochloride, but this usually acts very sluggishly. Thus, hemipinic acid readily yields *iso*vanillic acid, m. p. 255—257°.

A good proportion of the methyl is evolved as methyl chloride, but about one-third reacts with the base. J. C. W.

Keto-enol Isomerism. II. Ethyl Formylphenylacetate and Methyl Oxaloacetate. W. DIECKMANN (*Ber.*, 1916, **49**, 2213—2218). —Michael (A., 1912, i, 861) described a *β*-modification of ethyl formylphenylacetate, which Wislicenus (*ibid.*, 623) regarded as a mixture of the *α*- and *γ*-forms. It is now shown that it is the *γ*-ester contaminated with traces of alkali, and therefore more or less isomerised, the evidence being of the same nature as that put forward in the preceding paper (this vol., i, 833). What the equilibrium mixture in alcoholic solutions represents is still uncertain, and the author inclines to the view that it is not simply a keto-aldo equilibrium.

Methyl oxaloacetate was once obtained by Michael with m. p. 85—87°, instead of the usual m. p., 74—76° (A., 1906, i, 179). Here, again, it is found that the m. p. is influenced by traces of alkali, for the pure, alkali-free ester has m. p. 87—90° in Jena glass and 77° in soft glass. In this pure keto-form it may be preserved in Jena apparatus almost indefinitely; otherwise it is unstable. J. C. W.

The Anhydrides of *β*-*m*-Hydroxyphenylpropionic Acid. BERNHARD KNAKE and H. SALKOWSKI (*Ber.*, 1916, **49**, 2103—2107). —Some years ago an attempt was made to prepare *m*-ethylphenol by distilling *β*-*m*-hydroxyphenylpropionic acid, but the product was an anhydride, regarded at the time as an *ε*-lactone (Brebeck, *Diss.*, Munich, 1892). It has since then appeared to be more probable that the compound is an indene derivative, and this is rendered fairly certain by the fact that a hydroxyl group is still present in the molecule.

When β-*m*-hydroxyphenylpropionic acid is heated at 280—285° it forms a viscous, hygroscopic *anhydride*, according to the scheme $2C_9H_{10}O_3-H_2O$, but if quickly distilled it yields, in addition to the above anhydride, 5(or 7)-*hydroxy-α-hydrindone*,

$$OH\cdot C_6H_3<\begin{matrix}CH_2\\CO\end{matrix}>CH_2,$$

which separates in monoclinic crystals, m. p. 111°. This gives an *acetyl* derivative, m. p. 78°, a *diphenylcarbamate*, $C_9H_7O\cdot CO_2\cdot NPh_2$, pale yellow needles, m. p. 156°, and a *semicarbazone*, m. p. 243° (decomp.).

J. C. W.

Cyanohydrins and Amides. AUGUST ALBERT (*Ber.*, 1916, **49**, 1382—1385).—Many cyanohydrins can be prepared on the large scale by covering the aldehyde with a cold concentrated solution of sulphurous acid and then stirring in a solution of potassium cyanide. Another very useful method, applicable, for example, to *o*-nitrobenzaldehyde, consists in shaking a solution of the aldehyde in a solvent which does not mix with water or dissolve the cyanohydrin, with aqueous solutions of ammonium chloride and potassium cyanide, the reagents being in molecular proportions. The reaction stops at the hydroxy-cyanide stage instead of proceeding to the formation of the aminonitrile.

The hydrolysis of acylated cyanohydrins to the amides by means of acetic acid and zinc oxide was described by the author (*Habil.-schr.*, Munich, 1914) before the appearance of the paper by Aloy and Rabaut on the same subject (this vol., i, 263). *O*-Benzoyl-*o*-nitromandelamide, m. p. 129°, O-*acetyl*-o-*nitromandelamide*, $NO_2\cdot C_6H_4\cdot CH(OAc)\cdot CO\cdot NH_2$, m. p. 128°, and O-*acetyl*-3:4-*methylenedioxymandelamide*, m. p. 143°, have been prepared by this method, and the last-named amide has been further hydrolysed by boiling with dilute sodium carbonate to O-*acetyl*-3:4-*methylenedioxymandelic acid*, which forms prismatic rods, m. p. 161°.

J. C. W.

Action of Magnesium Aryl Haloids on Dicarboxylic Acids. W. DILTHEY and E. LAST (*J. pr. Chem.*, 1916, [ii], **94**, 49—52).—The constitution of the hydroxy-ketone, $OH\cdot CPh_2\cdot CH_2\cdot COPh$, obtained by the action of magnesium phenyl bromide on ethyl malonate (A., 1904, i, 667), is confirmed by the preparation of this compound by the interaction of ethyl benzoylacetate and magnesium phenyl bromide. In consequence of the ease with which the hydroxy-ketone (1) undergoes ketonic scission, yielding acetophenone and benzophenone, and (2) loses a molecule of water, giving phenyl phenylstyryl ketone, its acetyl derivative, oxime, and phenylhydrazone could not be prepared.

Phenylbenzylideneacetophenone [phenyl phenylstyryl ketone] has m. p. 89° (corr.); Kohler and Johnstin (A., 1905, i, 215) gave 92°. Its *oxime*, $CPh_2{:}CH\cdot CPh{:}NOH$, m. p. 141—147°, probably existing in isomeric forms, and its *phenylhydrazone*, m. p. 225—226° (corr.), and *semicarbazone*, m. p. 176° (corr.) were prepared.

The action of magnesium phenyl bromide on ethyl phenyl-

malonate yields, not the expected hydroxy-ketone, but a *carbinol*, $CPh_2:CPh\cdot CPh_2\cdot OH$ (?), which crystallises in yellow needles, m. p. 153° (corr.), and gives a Bordeaux-red solution in concentrated sulphuric acid. T. H. P.

Attempts to Synthesise Naringenin. W. MOSIMANN and J. TAMBOR (*Ber.*, 1916, **49**, 1700—1704).—The authors are of the opinion that Tutin's assumption that naringenin is 2:4:6-trihydroxyphenyl 4-hydroxystyryl ketone (2′:4′:6′:4-tetrahydroxychalkone) is correct, and have sought to prove this by synthesising the substance. Attempts to condense acetylphloroglucinol with *p*-hydroxybenzaldehyde have failed, and so the hydrolysis of various synthetic ethers by means of hydrobromic or hydriodic acid has been tried. So far, owing to the scarcity of materials, this method has also proved fruitless.

Acetylphloroglucinol dimethyl ether (2-hydroxy-4:6-dimethoxyacetophenone) condenses with *p*-hydroxybenzaldehyde in aqueous-alcoholic potassium hydroxide to form 2-*hydroxy*-4:6-*dimethoxyphenyl* 4-*hydroxystyryl ketone*,

$$OH\cdot C_6H_2(OMe)_2\cdot CO\cdot CH:CH\cdot C_6H_4\cdot OH,$$

which crystallises in bundles of small, orange-red needles, m. p. 188°, and yields a *diacetate*, in pale yellow needles, m. p. 147°. Similarly, 2:4:6-trimethoxyacetophenone forms 2:4:6-*trimethoxyphenyl* 4-*hydroxystyryl ketone*, in golden-yellow tetrahedra, m. p. 195—196°, which gives an *acetate*, in pale yellow rhombohedra, m. p. 108°.

These, and the corresponding tetramethoxy-compound, only gave amorphous products on demethylation, but 2-hydroxy-4:6-dimethoxyphenyl 4-methoxystyryl ketone (Kostanecki and Tambor, A., 1904, i, 426) yields a crystalline product on heating with acetic acid and fuming hydrobromic acid, which is most probably 2:4(or 6)-*diacetoxy*-6(or 4)-*methoxyphenyl* 4-*methoxystyryl ketone*,

$$OMe\cdot C_6H_2(OAc)_2\cdot CO\cdot CH:CH\cdot C_6H_4\cdot OMe;$$

it crystallises in bundles of slender, white needles, m. p. 157°.

Cyanomaclurin may be 2:4:6-trihydroxyphenyl 2:4-dihydroxystyryl ketone. The corresponding 2:4:6-*trimethoxyphenyl* 2:4-*dimethoxystyryl ketone* has been obtained by condensing 2:4:6-trimethoxyacetophenone with 2:4-dimethoxybenzaldehyde, in rosettes of pale yellow crystals, m. p. 127°, but attempts to hydrolyse it have failed. J. C. W.

Keto-enol Isomerism. I. The Supposed Existence of Isomerism with Keto-dibenzoylacetylmethane. W. DIECKMANN (*Ber.*, 1916, **49**, 2203—2213).—Attention is directed to the remarkable catalytic influence of traces of alkalis on the keto-enol equilibrium. Even the alkalinity of soft glass makes its influence felt, for the melting points of a number of compounds in which this tautomerism is possible are found to be very different if observed in Jena glass capillaries or soft glass tubes.

Thus, dibenzoylacetylmethane which has not come in contact with alkaline agents has the m. p. 150° in Jena glass tubes or as

low as 107—110° in soft glass. The higher m. p. is about that of the so-called γ-form obtained by Michael by heating the ketone with acetyl chloride (A., 1912, i, 632), and this is simply explained by the assumption that the chlorides of phosphorus so commonly present in this reagent remain as phosphoric acid with the ketone and so overcome the alkalinity of the glass when the m. p. is determined. Some experiments are described which show the influence of traces of alkalis (sodium acetate, etc.) or non-volatile acids on the m. p. of the ketone and on the titration value for the enol present after melting. The same catalytic influence of alkalis is observed in the reverse process, the change from enol to ketone. If the enol is precipitated by hydrochloric acid instead of by acetic acid (which is usual) it is obtained free from alkali, and then has the m. p. 85° in Jena glass capillaries and remains enolic for a considerable time at 85—95° under these conditions.

Michael's stereoisomeric ketone forms of dibenzoylacetylmethane are therefore non-existent. There is only one form. In the case of tribenzoylmethane, Michael did not observe different modifications, but this is again influenced by alkalis as above. The alkali-free ketone in Jena glass tubes has the m. p. 245—250°, but this may be as low as 230° in soft glass. The alkali-free enol has m. p. 155°, is stable in the cold, but changes within an hour at 100° into the ketone, more rapidly in a soft glass tube. J. C. W.

Quinhydrones. I. LIFSCHITZ (*Ber.*, 1916, **49**, 2050—2054).—The author is engaged on a study of the optical properties of various classes of additive compounds. Quinhydrones are found to behave very differently from dyes or from *meri*-quinonoid additive compounds (compare Hantzsch, this vol., i, 431), and, moreover, the absorption spectrum of benzoquinhydrone is by no means typical of the class. This is demonstrated by studying the effect of adding hexamethylbenzene to chloranil. The particular band of the chloranil (ultra-violet) is flattended more and more as the hydrocarbon is added, and a new "quinhydrone band" appears in the visible spectrum almost as intense as a dye band. The equilibrium, quinhydrone $\rightleftarrows$ quinone + hydrocarbon, might even be studied spectrographically. In the case of benzoquinhydrone, the bands due to the quinone and the additive compound are apparently so near as to overlap. In such cases, therefore, the quinhydrone curve should be carefully compared with those of its components. J. C. W.

1 : 3-Dibromoanthraquinone. FRITZ ULLMANN and OSKAR EISER (*Ber.*, 1916, **49**, 2154—2169).—The bromine atom in position 1 in 1 : 3-dibromoanthraquinone is very labile, and a number of reactions in which it participates are described. The other bromine atom also enters into reaction at higher temperatures, and further examples of this type of change are given. Similarly, the bromine atom in position 4 of 2 : 4-dibromo-1-aminoanthraquinone is shown to be reactive. Condensations of 1 : 3-dibromo-2-aminoanthraquinone with mercaptans are also described.

1 : 3-Dibromo-2-aminoanthraquinone is deprived of the amino-group by the diazo-reaction when 1 : 3-*dibromoanthraquinone* is obtained in 98% yield as canary-yellow needles, m. p. 210° (corr.). This reacts with *p*-toluenesulphonamide in boiling amyl alcohol, in the presence of anhydrous potassium acetate and a little copper acetate, to form 3-*bromo*-1-p-*toluenesulphonylaminoanthraquinone*, in pale greenish-yellow needles, m. p. 227°, which yields on hydrolysis 3-*bromo*-1-*aminoanthraquinone*, in glistening, red needles, m. p. 243°, the *acetyl* derivative of which forms yellow needles, m. p. 214° (corr.). 3-*Bromo*-1-*anilinoanthraquinone* is obtained by a similar condensation, in red needles, m. p. 175° (corr.), whilst anthranilic acid yields in the same way 3-*bromo*-1-*anthraquinonyl-anthranilic acid* (I), in brick-red, glistening needles, m. p. 271° (corr.). When the chloride of this acid is heated in nitrobenzene, it gives 3-*bromoanthraquinone*-2 : 1-*acridone* (4-*bromo*-1 : 2-*phthaloylacridone*) (II), which forms glistening, reddish-violet crystals, m. p. 303°, and is transformed into a *dibromo*-compound, m. p. 298°, on boiling with bromine and nitrobenzene.

$$C_6H_4{<}\substack{CO\\CO}{>}C_6H_2Br\cdot NH\cdot C_6H_4\cdot CO_2H \longrightarrow$$

(I.)

$$C_6H_4{<}\substack{CO\\CO}{>}C_6HBr{<}\substack{NH\\CO}{>}C_6H_4$$

(II.)

3 : 3′-*Dibromo*-1 : 1′-*dianthraquinonyl*,

$$C_6H_4{<}\substack{CO\\CO}{>}C_6H_2Br\cdot C_6H_2Br{<}\substack{CO\\CO}{>}C_6H_4,$$

is obtained in yellow needles, m. p. 395°, by boiling the 1 : 3-dibromoanthraquinone with copper powder in nitrobenzene.

1 : 3-*Diphenoxyanthraquinone* is prepared in yellow needles, m. p. 167°, by boiling the dibromo-compound with potassium phenoxide and phenol in the presence of copper powder. Similarly, 1-aminoanthraquinone condenses in naphthalene at 230°, in the presence of potassium acetate and copper acetate, to form 1 : 3-*di*-1′-*anthraquinonylaminoanthraquinone*,

$$C_6H_4{<}\substack{CO\\CO}{>}C_6H_2\left(NH\cdot C_6H_3{<}\substack{CO\\CO}{>}C_6H_4\right)_2,$$

which crystallises in brick-red leaflets, m. p. above 400°.

1 : 3-Dibromo-2-aminoanthraquinone condenses with *p*-thiocresol to form 3-*bromo*-2-*amino*-1-*anthraquinonyl* p-*tolyl sulphide* (III), in dichroic, red crystals, m. p. 188° (corr.), and this is converted by treatment with concentrated sulphuric acid and formaldehyde into 5-*bromo*-3 : 12-*dimethyl*-(1 : 2)-*anthraquinonylbenzothiazine* (IV), in glistening, yellow needles, m. p. 327°.

$$C_6H_4{<}\substack{CO\\CO}{>}C_6HBr(NH_2)\cdot S\cdot C_6H_4Me \longrightarrow$$

(III.)

$$C_6H_4{<}\substack{CO\\CO}{>}C_6HBr{<}\substack{S\\NMe}{>}C_6H_3Me$$

(IV.)

1-Aminoanthraquinone is most conveniently brominated by boiling it with bromine in nitrobenzene. 2:4-Dibromo-1-aminoanthraquinone (D.R.-P., 115048) yields 2-bromo-1-aminoanthraquinone (D.R.-P., 160169, 261270) when heated with concentrated sulphuric acid and aniline at 160—190°, and condenses with *p*-toluenesulphonamide to form *2-bromo-1-amino-4-*p*-toluenesulphonylaminoanthraquinone*, which crystallises in reddish-brown leaflets, and is hydrolysed by hot concentrated sulphuric acid to *2-bromo-1:4-diaminoanthraquinone*, violet crystals with metallic lustre, m. p. 234°. The base also condenses with anthranilic acid to form *3-bromo-4-amino-1-anthraquinonylanthranilic acid*, in felted, blue needles, m. p. 276°, and this undergoes further reaction with chlorosulphonic acid, resulting in the formation of *3-bromo-4-amino-1:2:1′:2′-anthraquinoneacridone* (*4-bromo-3-amino-1 : 2-phthaloylacridone*), $C_6H_4<{CO \atop CO}>C_6Br(NH_2)<{NH \atop CO}>C_6H_4$, in dark blue needles (D.R.-P., 256626). Finally, the base condenses with potassium phenoxide to form *1-amino-2:4-diphenoxyanthraquinone*, glistening, yellow needles, m. p. 184°, mixed with a small amount of *4-phenoxy-2:1-anthraquinone-2′:1′-phenoxazine*,

$$C_6H_4<{CO \atop CO}>C_6H(OPh)<{NH \atop -O-}>C_6H_4,$$

which forms glistening, dark blue crystals, m. p. 428°. J. C. W.

Formula of β-Santolinenone. L. Francesconi and N. Granata (*Gazzetta*, 1916, **46**, ii, 251—256. Compare A., 1914, i, 1134, 1202).—β-Santolinenone, contained in the essential oil of *Santolina chamæcyparissus*, gives a liquid oxime and a simple *hydroxylamine*, m. p. 63—64°, which emits bubbles at 179°, turns yellow at 192°, is optically inactive, and reduces Fehling's solution, slowly in the cold and rapidly when heated. Under the action of acid, the oxime is reconverted into the ketone, but the hydroxylamine is stable, and thus resembles the majority of simple hydroxylamines. This β-hydroxylamine yields an *oxalate*, $C_{10}H_{16}O,NH_3O,H_2C_2O_4$, which forms white tufts, m. p. 161° (decomp.), and is inactive. Oxidation of the β-hydroxylamine by means of mercuric oxide gives a white, crystalline nitroso-compound, m. p. 60—62°, which turns blue when fused, is highly volatile at the ordinary temperature, and has a pungent odour similar to that of the ketone.

The behaviour of β-santolinenone is best expressed by the formula

$$CMe_2{:}C<{CO\cdot CHMe \atop CH_2-CH_2}>CH_2 \quad \text{or} \quad CMe_2{:}C<{CH_2\cdot CHMe \atop CO——CH_2}>CH_2.$$

T. H. P.

Artificial Resin Acids. Georg Cohn (*Chem. Zeit.*, 1916, **40**, 725—727).—The condensation of formaldehyde with phenoxyacetic acids in presence of hydrochloric acid gives rise to resins with strong acidic properties. Thus from phenoxyacetic acid itself a hard, pale yellow resin was produced. It gives a red coloration with

concentrated sulphuric acid and an amorphous, brown colouring matter with resorcinol and zinc chloride, showing strong fluorescence in alkaline solution. The ammonium salt is neutral in reaction, and gives with salts of the heavy metals flocculent precipitates, and with dyes, such as magenta, methylene-blue, etc., coloured precipitates on the addition of acetic acid. Alkaloids are similarly precipitated, and can be detected in the precipitate of resin acid. On heating at 140° the resin acid loses water and formaldehyde, and is converted into a brittle and less soluble resin. When trioxymethylene is used for the preparation instead of formaldehyde the product is a white powder which does not soften on the water-bath and is less soluble than the above, and a somewhat similar product is formed by the action of chloroacetic acid on the condensation product of phenol with formaldehyde. Resin acids prepared from resorcinol, guaiacol, carvacrol, and eugenol are also described. α-Naphthol gave, on the other hand, a crystalline product, m. p. 227—228°. G. F. M.

Colophony and Abietic Acid. GEORG COHN (*Chem. Zeit.*, 1916, **40**, 791—792).—Colophony resin is almost entirely soluble in ammonia, and the solution possesses properties similar to those of the ammonium salts of the previously described artificial resin acids (preceding abstract) in precipitating basic dyes and alkaloids from their solutions. The copper salt, although insoluble in ammonia and in alcohol, is readily soluble in ether. Under certain conditions colophony resin gives almost solid gels in aqueous ammonia up to dilutions as great as 1 in 500. Other bases, such as piperidine, give gels of a similar nature. A technically pure abietic acid of m. p. 156—162° was readily obtained in 56% yield from white colophony by warming on the water-bath with an equal weight of pure methyl alcohol and about an eighth of its weight of concentrated sulphuric acid with constant shaking. Two layers were rapidly formed and the whole set to a crystalline mass, which was filtered and washed with methyl alcohol. Abietic acid resembles the higher fatty acids in its behaviour with alkali hydroxides in regard to gel formation. The author is of opinion that natural colophony is a more or less pure, glassy abietic acid, and not an anhydride, as has been suggested. G. F. M.

Storax. I. Identification of Conifer Resin Acids (Abietic and Pimaric Acids). M. HENZE (*Ber.*, 1916, **49**, 1622—1632).—In the most recent investigation of storax, Tschirch and van Itallie (A., 1902, i, 109) apparently regarded the resin contained in the balsam as an individual ester, compounded of cinnamic acid and "storesinol." It is now found that the resin consists of five or six compounds, the chief being free abietic and *d*-pimaric acids, a ketone and an easily esterifiable alcohol. The production of these acids was hitherto regarded as peculiar to the conifers, but it is possible that the resins obtained by wounding trees belonging to many other families contain them also.

For the isolation of the acids, storax is dissolved in 70—80% alcohol, and the solution, decanted from a dark oil, is heated and

mixed with lead acetate. The lead salts crystallise on cooling, and are dried, recrystallised from chloroform and ethyl acetate, and decomposed by glacial acetic acid. On pouring into water, the acids are precipitated and they are then fractionally crystallised from acetic acid mixed with acetone or methyl alcohol. *d*-Pimaric acid separates first in rectangular platelets or columns, m. p. 210—211° (sodium salt, pearly platelets; ammonium salt, silky needles; silver salt analysed), whilst abietic acid, the main constituent, crystallises later in triangular platelets, m. p. 158—165° (sodium salt, amorphous; ammonium salt, a jelly; lithium salt, fine crystals; silver salt analysed).

Both acids suffer decomposition on distillation into carbon dioxide and aliphatic acids (? *iso*butyric acid), but pimaric acid distils unchanged in a vacuum. J. C. W.

Hydrolysis of Picrotoxin by Methyl-alcoholic Potassium Hydroxide. Picrotoxinic Acid. Paul Horrmann and Hans Wächter (*Ber.*, 1916, **49**, 1554—1567. Compare this vol., i, 566).—Now that the products of the hydrolysis of picrotoxinin and picrotin have been characterised, it is possible to investigate the action of methyl-alcoholic potassium hydroxide on picrotoxin. The products are recognised to be potassium β-picrotinate, methyl hydrogen picrotoxinindicarboxylate, and the esters of picrotoxinic and α-picrotinic acids. The hydrogenation and ozonation of picrotoxinic acid are also described. The ozonide yields formic acid and a ketonic acid on hydrolysis, and as the latter, "picrotoxinonic acid," gives a dibasic acid with the same number of carbon atoms on oxidation with nitric acid, it cannot be an α-ketonic acid, and picrotoxinic acid cannot be of the type $CH_2{:}CR{\cdot}CO_2H$. The ketonic acid probably contains the carbonyl group in a ring, and its oxidation product is probably a lactone, thus:

$$\begin{matrix}OH\\CO_2H\end{matrix}\!\!>C_{11}H_{12}O_4<\!\!\begin{matrix}CO\\|\\CH_2\end{matrix} \xrightarrow[-H_2O]{+3O} (CO_2H)_2C_{11}H_{12}O_4<\!\!\begin{matrix}O\\|\\CO\end{matrix}.$$

Picrotoxinic acid forms an *acetyl* derivative, $C_{17}H_{20}O_8$, m. p. 206°, and this gives a *silver* salt, $C_{17}H_{19}O_8Ag,2H_2O$. *Dihydropicrotoxinic acid*, $C_{15}H_{20}O_7,H_2O$, is prepared by the hydrogenation of picrotoxinic acid in the presence of palladous chloride; it crystallises in long, slender needles, m. p. 252°, $[\alpha]_D^{17.5°} + 94°53'$, and forms a *methyl* ester, long, stout needles, m. p. 205°, $[\alpha]_D^{17.5°} + 70°16'$, and an *ethyl* ester, long, slender needles, m. p. 170°, $[\alpha]_D^{17.5°} + 70°51'$. Anhydrous picrotoxinic acid dissolved in ethyl acetate and treated with ozone until it no longer absorbs bromine, forms an *ozonide*, $C_{15}H_{18}O_{10}$, and this yields *picrotoxinonic acid*, $C_{14}H_{16}O_8$, on boiling with water. This acid crystallises from water in long prisms which crumble to a powder in the air, and the anhydrous substance decomposes at 260°, has $[\alpha]_D^{17.5°} + 102°23'$, and forms a *semicarbazone*,

$$C_{15}H_{19}O_8N_3,2H_2O,$$

decomp. 197°, an *oxime*, $C_{14}H_{16}O_7{:}N{\cdot}OH$, decomp. 206°, and a phenylhydrazine *salt* of a *phenylhydrazone*,

$$C_{14}H_{16}O_7{:}N{\cdot}NHPh,NH_2{\cdot}NHPh,$$

pale yellow needles, decomp. 207°. The acid also gives a *compound*, $C_{14}H_{10}O_5$, decomp. above 300°, when heated at 250° in a vacuum, and yields a *methyl ester* of its *methyl ether*, $C_{16}H_{20}O_8$, when boiled with methyl iodide and silver oxide. This compound has m. p. 157°, $[\alpha]_D^{17.5°}+111°30'$, forms a *semicarbazone*, glistening, prismatic tablets, decomp. 239°, and may be hydrolysed to the *methyl ether* of picrotoxinonic acid, which crystallises in stout needles, m. p. 185°, $[\alpha]_D^{17.5°}+108°30'$, and forms a *phenylhydrazone*, in yellow needles, decomp. 211°. When heated with concentrated nitric acid, picrotoxinonic acid yields a dibasic *acid*, $C_{14}H_{14}O_{10}$, which crystallises in stout prisms, decomp. about 300°, $[\alpha]_D^{17.5°}+76°59'$, and forms *silver* and *barium* salts. J. C. W.

Constitution of Picrotic Acid, $C_{15}H_{18}O_4$. I. Degradation of the Acid to an Aldehyde, $C_{12}H_{12}O_3$. PAUL HORRMANN (*Ber.*, 1916, **49**, 2107—2116).—Picrotic acid has been converted through the amide into the amine, $C_{14}H_{17}O_2{\cdot}NH_2$, and this has been degraded by Hofmann's method to a tertiary base, $C_{14}H_{17}O_2{\cdot}NMe_2$, and a neutral substance, $C_{14}H_{16}O_2$. The latter has also been converted into an ozonide which yields an aldehyde, $C_{12}H_{12}O_3$, on hydrolysis. The neutral substance may therefore be represented by the formula $C_{11}H_{11}O_2{\cdot}CH{:}CHMe$, and picrotic acid is consequently a butyric acid substituted by the residue, $C_{11}H_{11}O_2$. This agrees with the facts gathered during researches on the oxidation of the acid, which have pointed to the fact that the benzene nucleus in the acid contains only two oxidisable substituents, one a methyl group and the other a chain with four carbon atoms (compare this vol., i, 566).

Picrotic acid contains a carboxyl and a lactone group. It is converted into the chloride by means of phosphorus pentachloride and then into the *amide*, $C_{14}H_{17}O_2{\cdot}CO{\cdot}NH_2$, which crystallises in needles, m. p. 138°, and, on distillation, yields the *nitrile*, $C_{14}H_{17}O_2{\cdot}CN$, in stout crystals, m. p. 80°, b. p. 223°/12 mm. The amide is transformed by treatment with concentrated sodium hypochlorite into the *amine*, $C_{14}H_{17}O_2{\cdot}NH_2$, which is a viscous liquid, b. p. 200·5°/10 mm., and forms a *hydrochloride*, $1H_2O$, in stout, rhombohedra, a *platinichloride*, stout prisms, decomp. 229°, and a *picrate*, $1H_2O$, needles, m. p. 198°. The corresponding quaternary ammonium base, $C_{14}H_{17}O_2{\cdot}NMe_3{\cdot}OH$, forms an *iodide*, $1H_2O$, in stout prisms, m. p. 149°, and a *perchlorate*, in feathery needles, m. p. 235°, and is decomposed at 190—220° into the tert.-*base*, $C_{14}H_{17}O_2{\cdot}NMe_2$, b. p. 196°/10 mm. [*platinichloride*, orange needles, m. p. 223° (decomp.); *aurichloride*, stout prisms, m. p. 160°], and the unsaturated *compound*, $C_{14}H_{16}O_2$, b. p. 172—183°/13 mm. The latter is saturated with ozone in ethyl acetate and the ozonide is warmed with barium carbonate and water, when the *aldehyde*, $C_{12}H_{12}O_3$, is produced. This crystallises in large leaflets, which sublime in large tablets at above 140°/14 mm. and boil at 195°/14 mm. The *semicarbazone* crystallises in slender needles, m. p. 256° (decomp.), and the *phenylhydrazone* in pale yellow needles, m. p. 236°. J. C. W.

Bixin. III. I. J. RINKES and J. F. B. VAN HASSELT (*Chem. Weekblad*, 1916, **13**, 1224—1229. Compare this vol., i, 495).—Distillation in an absolute vacuum of the liquid obtained by the action of water on the ozonide of methylbixin yields four products. The first is a liquid distilling below 60° and forming a semicarbazone, m. p. 261° (not 249°, as previously stated). Between 60° and 70° the product is the crystalline methyl β-acetylacrylate (not acetyl-γ-butyrolactone, as previously supposed), which yields the following derivatives: oxime, m. p. 100°; semicarbazone, m. p. 196°; *p*-nitrophenylhydrazone, m. p. 227—228°; phenylhydrazone, m. p. 156°; β-acetoximoacrylamide, m. p. 233°. Between 110° and 120° the product is a crystalline compound, $C_8H_{10}O_3$, m. p. 85°, probably the methyl ester of a ketonic acid. Its oxime has m. p. 106°. Between 120° and 130° there distils an oil, which yields an almost insoluble semicarbazone, m. p. 256°. The experiments indicate that methylbixin contains the grouping $\overset{\shortparallel}{C}Me{\cdot}CH{:}CH{\cdot}\overset{\shortparallel}{C}{\cdot}OMe$. A. J. W.

The Pigments of Molasses and the Residues from the Extraction of Sugar from Molasses. I. H. STOLTZENBERG (*Ber.*, 1916, **49**, 2021—2023).—Molasses and similar residues from the beet-sugar industry contain a fluorescent pigment which is soluble in alcohol, and a dark brown one which is insoluble. The latter has been isolated from the residue left after extracting a syrup with alcohol, by precipitation with lead acetate and decomposition of the precipitate by means of hydrogen sulphide. The *pigment*, $C_{20}H_{24}O_9N_2$, is a dark brown powder, soluble in alkalis or ammonia solution and in concentrated hydrochloric acid, but only sparingly so in water or other hydroxylic solvents. It sinters at 178—180° and is tasteless. Its behaviour on oxidation and reduction is briefly mentioned, but these questions and the nature of the other nitrogenous products in the syrup (the lead precipitate represents only one-third of the nitrogen) will apparently be dealt with in future papers. One kilo. of molasses yields about 1·2 grams of the pigment. J. C. W.

Pyrylium Compounds. WALTHER DILTHEY (*J. pr. Chem.*, 1916, [ii], **94**, 53—76).—The author has obtained derivatives of the pyrylium ring by a method which, when ammonia is present, leads to pyridine derivatives. It is therefore considered probable that syntheses which give the latter consist initially in formation of the pyrylium ring, the pyridine ring being formed later under the influence of ammonia. The most readily accessible salt is the stable double salt of triphenylpyryl chloride and ferric chloride, and is obtained from acetophenone (2 mols.), benzaldehyde (1 mol.) [or phenyl styryl ketone (1 mol.) and acetophenone (1 mol.)], acetic anhydride, and ferric chloride; benzylidenediacetophenone is formed as intermediate product. That the triphenylpyryl chloride here obtained is the 2:4:6-compound is shown by the ready formation from it, by the action of ammonia, of 2:4:6-triphenylpyridine. Similarly, the interaction of acetophenone and acetic anhydride in presence of ferric chloride yields 2:6-diphenyl-4-methylpyryl

chloride, which is converted by ammonia into 2:6-diphenyl-4-methylpyridine.

For the colourless pseudo-base or pyranol obtained from 2:4:6-triphenylpyryl chloride by the action of a non-nitrogenous alkali, several constitutions are possible, the most probable being

$$CPh \lessdot \begin{matrix} CH{=\!=\!=}CPh \\ CH\cdot CPh(OH) \end{matrix} \gtrdot O.$$

Triphenylpyrylium compounds are discussed in comparison with those of triphenylmethyl, distyryl ketone, triphenylpyridine, and benzopyrylium, the last name being suggested in place of Decker and von Fellenberg's phenopyrylium (A., 1907, i, 950; 1909, i, 116), which resembles phenylpyrylium so closely as to lead to confusion. Decker and von Fellenberg's constitution for triphenylpyrylium is regarded as the most probable.

The *double* compound of 2:4:6-*triphenylpyryl chloride* and *ferric chloride*, $CPh \lessdot \begin{matrix} CH{:}CPh \\ CH\cdot CPh \end{matrix} \gtrdot OCl,FeCl_3$, forms yellowish-red needles, m. p. 277° (corr.).

2:4:6-*Triphenyl-2-pyranol*, $C_{23}H_{18}O_2$, forms bundles of colourless needles, m. p. 119° (corr.), and exhibits faint fluorescence in glacial acetic acid solution and intense bluish-green fluorescence in solution in concentrated sulphuric acid. Crystallisation of pyranol, especially from pyridine, is accompanied by the precipitation of a sparingly soluble substance, which shows no fluorescence in sulphuric acid, and is possibly the ether corresponding with the pyranol. The *platinichloride*, $(C_{23}H_{17}OCl)_2,PtCl_4$, forms a yellow precipitate, m. p. 225—226° (corr.).

2:4:6-*Triphenylpyryl picrate*, $C_{23}H_{17}O\cdot O\cdot C_6H_2(NO_2)_3$, forms stout, deep red prisms, m. p. 226—227° (corr.), and has a yellowish-red streak. With excess of picric acid in ether or acetone, this salt yields the *acid picrate*, $C_{29}H_{19}O_8N_3,C_6H_3O_7N_3$, which crystallises in yellow needles, m. p. 186—187° (corr.), and loses the extra molecule of picric acid when treated with a solvent of the latter.

αγε-Triphenyl-Δ^{β}-pentene-αε-dionedisemicarbazone,

$$NH_2\cdot CO\cdot NH\cdot N{:}CPh\cdot CH_2\cdot CPh{:}CH\cdot CPh{:}N\cdot NH\cdot CO\cdot NH_2,$$

prepared from 2:4:6-triphenyl-2-pyranol (1 mol.) and semicarbazide hydrochloride (2 mols.) in pyridine, forms short, white needles, m. p. 225° (corr.) (decomp.), and gives a yellow, non-fluorescent solution in concentrated sulphuric acid.

2:6-*Diphenyl-4-methylpyryl chloride*, $C_{18}H_{15}OCl,H_2O$, forms long, straw-yellow needles, m. p. 125—126° (corr.; decomp.), and shows faint blue fluorescence in solution in a large amount of water or in sulphuric acid. With ferric chloride, it forms the *double* salt, $C_{18}H_{15}OCl,FeCl_3$, which separates in long, brownish-yellow, lanceolate crystals, m. p. 175° (corr.), and also shows slight blue fluorescence in aqueous or sulphuric acid solution.

2:6-*Diphenyl-4-methylpyridine*, $C_{18}H_{15}N$, forms hedgehog-like aggregates of colourless, lanceolate crystals, m. p. 72—73°, and functions as a weak base, but gives well-crystallisable salts. The *nitrate*, m. p. 185° (corr.), and *picrate*, m. p. 212—213° (corr.), were analysed.

2:6-*Di*-p-*anisyl*-4-*methylpyryl chloride* is obtained as double salt with *ferric chloride*, $CMe\lessgtr\begin{matrix}CH:C(C_6H_4\cdot OMe)\\CH\cdot C(C_6H_4\cdot OMe)\end{matrix}\gtrless OCl,FeCl_3$, when *p*-methoxyacetophenone is treated with acetic anhydride and ferric chloride. The double salt crystallises in brown needles with blue lustre, or in slender, brownish-yellow, rectangular prisms, m. p. 179—180° (corr.), and gives a yellow solution with marked yellowish-green fluorescence in concentrated sulphuric acid.

T. H. P.

Hydroxychalkones. J. TAMBOR [with A. ECKMANN and H BERNER (*Ber.*, 1916, **49**, 1704—1711).—Since so many plant pigments have been recognised as hydroxy-flavanones, -flavones, -flavanols, or -chalkones, syntheses of these compounds have acquired more interest, and it is proposed to pursue the subject further.

Resacetophenone and *m*-hydroxybenzaldehyde condense together in the presence of aqueous-alcoholic potassium hydroxide to form 2 4-*dihydroxyphenyl* 3-hydroxystyryl

$$OH\cdot C_6H_4\cdot CH:\quad\cdot CO\cdot C_6H_3(OH)_2,$$

which crystallises in microscopic, brick-red needles, m. p. 209°, and yields a triacetate, in pale yellow needles, m. p. 100°. The crude dibromide of this, on warming with 40% potassium hydroxide, yields 7:3′-*dihydroxy*-2-*phenyl*-γ-*benzopyrone*,

$$OH\cdot C_6H_3<\begin{matrix}O—C\cdot C_6H_4\cdot OH\\ \quad || \\CO\cdot CH\end{matrix},H_2O,$$

which crystallises in pale yellow needles, m. p. 267°, and is apparently identical with Harpe and Kostanecki's 3:3′-derivative, for it gives the same diethoxy-compound, m. p. 153° (A., 1900, i, 238). The corresponding 7:3′-*dihydroxy*-2-*phenyl*-2:3-di'hydro-y-b*enzo*-pyrone (7:3′-*dihydroxyflavanone*) is obtained by heating the above trihydroxychalkone with 10% sulphuric acid; it has m. p. 182—183°, and forms a *diacetate*, m. p. 92—93°.

m-Methoxybenzaldehyde condenses with resacetophenone dimethyl ether to form 2:4-*dimethoxyphenyl* 3-*methoxystyryl* ketone, which crystallises in pale yellow scales, m. p. 68°.

Resacetophenone also condenses with *p*-hydroxybenzaldehyde, yielding 2:4-*dihydroxyphenyl* 4-Ji ydroxystyryl ketone, in yellowish-red needles, m. p. 187—188°, and this forms a triacetate, m. p. 123°, and a *trimethoxy*-compound, m. p. 89°. The acetate combines with bromine to form 2:4-*diacetoxyphenyl* αβ-*dibromo*-β-4-*acetoxyphenylethyl* ketone, m. p. 172—173°, which is converted into 7:4′-*dihydroxy*-2-*phenyl*-y-*benzopyrone*, a glistening, yellow powder, m. p. 315°, identical with Kostanecki and Osius's 3:4′-derivative (A., 1899, i, 370). This yields a dimethoxy-compound, m. p. 143—144°. The chalkone may also be converted into the flavanone, 7:4′-*di*hydroxy-2-ph*enyl*-2:3-*dihydro*-y-b*enzopyrone*, $C_{15}H_{12}O_4,H_2O$, which crystallises in yellow needles, m. p. 182—183°, and forms a *diacetate*, in silky, white needles, m. p. 175—176°.

J C. W.

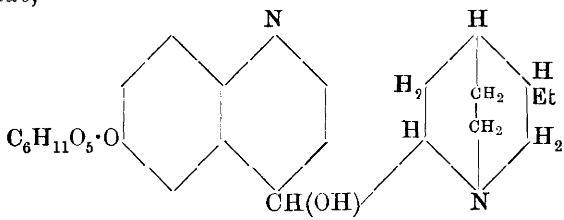
Action of Sulphur on Octylene under Pressure. WALTER FRIEDMANN (*Ber.*, 1916, **49**, 1551—1554).—When caprylene [n-Δ^{β}-octene] is heated with sulphur under pressure at 270—280° for a day, the following compounds are formed: the thiophen compound, $C_8H_{12}S$, b. p. 180°, and the dimethylthiophthen derivative, $C_8H_8S_2$, m. p. 116—117°, which are obtained from n-octane under the same conditions (this vol., i, 735); a *dimethyldiamylthiophen*, $C_{16}H_{28}S$, b. p. 160—162°/11 mm.; and a *compound*, $C_{24}H_{38}S_2$, a yellowish-red, heavy oil, b. p. 186—188°/11 mm., D^{20} 0·966. J. C. W.

Dissociation Constants of Some Alkaloids. G. VON WEISSE and MEYER LÉVY (*J. Chim. phys.*, 1916, **14**, 261—284).—The relative strengths and dissociation constants of a number of alkaloids have been determined by the method of Dutoit and Duboux. Neutralisation curves and displacement curves are produced, and from them the dissociation constant is calculated. The former curves are obtained by measuring the conductivity of a solution of an alkaloid and then adding measured volumes of normal hydrochloric acid until the solution is neutralised, and measuring the electrical conductivity after each addition. The conductivities are then plotted against the number of c.c. of acid added. The displacement curves are produced similarly, using a solution of a salt of the alkaloid and adding measurable quantities of N-sodium hydroxide. The method of calculation of the dissociation constant is given for the following cases: (1) From neutralisation curves. (*a*) Monacid bases the hydrochlorides of which are not hydrolysed; (*b*) monacid bases the hydrochlorides of which are partly hydrolysed; (*c*) monacid bases the hydrochlorides of which are strongly hydrolysed. (2) From displacement curves: diacid bases. The following values of K, the dissociation constant, have been determined at 18°: piperidine, $1·3 \times 10^{-3}$; coniine, $1·0 \times 10^{-3}$; conhydrine, *ca.* $2·0 \times 10^{-4}$; piperine, $1·0 \times 10^{-14}$; strychnine, *ca.* $1·0 \times 10^{-7}$; brucine, $1·0 \times 10^{-7}$; codeine, *ca.* $1·0 \times 10^{-7}$; narceine, *ca.* $1·0 \times 10^{-7}$; pilocarpine, *ca.* 10^{-7}; atropine, $1·7 \times 10^{-12}$; hyoscyamine, $1·9 \times 10^{-12}$; theophylline, $1·2 \times 10^{-14}$; caffeine, $0·7 \times 10^{-14}$; sparteine I, $1·0 \times 10^{-2}$; sparteine, *ca.* 10^{-6}; lupinine, 2×10^{-5}; colchicine, *ca.* 10^{-14}; emetine, $5·0 \times 10^{-7}$. J. F. S.

The *d*-Glucoside of Dihydrocupreine. P. KARRER (*Ber.*, 1916, **49**, 1644—1648).—It has sometimes been affirmed that glucosides are more physiologically active than their parent substances, but that is certainly not so in the case of dihydrocupreine *d*-glucoside.

For the production of this compound, the alkaloid is treated with acetobromoglucose in the presence of dilute sodium hydroxide, whereby the *tetra-acetyl*-d-*glucoside* is obtained as an amorphous powder, m. p. 95—102° (*hydrochloride*, 2HCl, well-developed needles, m. p. 236—237°, $[\alpha]_D^{18} - 1·88°$), and this is hydrolysed by

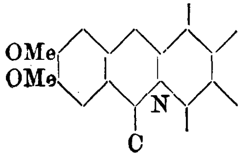
contact with $0{\cdot}5N$-sodium hydroxide to the *dihydrocupreine* d-*glucoside*,



This is also amorphous, has m. p. about 160°, and forms a *hydrochloride*, $[\alpha]_D^{20}$ about $-160°$. J. C. W.

Pure Colchicine. E. MERCK (*Pharm. Zentr-h.*, 1916, **57**, 619—620).—Pure colchicine forms white, amorphous, odourless flakes, m. p. between 142° and 147°. It is readily soluble in water, alcohol, chloroform, or benzene. From its aqueous solution, it is deposited in large, yellow, rhombic crystals of the sparingly soluble hydrate of the formula $(C_{22}H_{25}O_6N)_2,3H_2O$. Colchicine forms also two crystalline compounds with chloroform, containing respectively 1 and 2 mols. combined with 1 mol. of chloroform. They are completely decomposed at 100°, or by warming in aqueous solution at 50°, in the latter case with formation of the hydrate. G. F. M.

The Alkaloids of Ipecacuanha. P. KARRER (*Ber.*, 1916, **49**, 2057—2079).—Working independently, and with other ends in view, the author has obtained evidence as to the chemistry of emetine and cephaeline which agrees almost entirely with that put forward by Carr and Pyman (T., 1914, **105**, 1591). He also has shown that emetine is the *O*-methyl ether of cephaeline, and has prepared, in addition, other ethers. Of the methyl, ethyl, and propyl ethers, the first-named, that is, emetine, is always the most physiologically active, which is contrary to the rule in the case of homologues of quinine or hydroquinine. It is also shown that emetine and cephaeline yield the same product on demethylation, and this is designated emetoline, because of its phenolic character. Evidence as to the nitrogen linkings has been obtained by the Hofmann degradation, and it appears that one of the atoms is in a simple ring, whilst the other is common to two nuclei. Emetine also yields a yellow product on oxidation with iodine. In these respects, therefore, it greatly resembles canadine, that is, hydrogenated berberine. All the facts known at present in relation to emetine point to the presence in the molecule of the annexed fragment.



A historical summary of the chemistry of the ipecacuanha alkaloids is given. The properties and analyses of emetine and its hydrochloride and very characteristic hydriodide, and of cephaeline hydrochloride, are described.

Emetine hydrochloride is demethylated by boiling with hydriodic acid and red phosphorus, and *emetoline* (*noremetine*), $C_{25}H_{32}O_4N_2$, is thus produced, in pale yellow flocks, m. p. 205°, which give the catechol reaction with ferric chloride. Cephaeline gives the same compound.

Cephaeline may be methylated by means of methyl sulphate, but a better agent is nascent diazomethane, obtained by adding nitrosomethylurethane to a solution of the hydrochloride in methyl alcohol and shaking the mixture with methyl-alcoholic potassium hydroxide. *Emetethyline* (*cephaeline ethyl ether*), m. p. 68—71°, forms a *hydriodide*, $C_{30}H_{42}O_4N_2,2HI$, in white clusters, m. p. 209—210°; *emetpropyline*, m. p. 58—60°, forms a *hydrochloride*, 2HCl, in velvety needles; *emetallyline hydrochloride* crystallises in white needles.

When emetine is methylated, it yields *N*-methylemetine dimethiodide, $C_{32}H_{48}O_4N_2I_2$, and this, on boiling with silver oxide and water, yields a product derived from the base through the elimination of two molecules of water. This *anhydrotrimethylemetine* is a vitreous substance, b. p. 283—284°/3 mm., which forms a *hydrochloride*, $C_{29}H_{37}O_4N_2Me_3,2HCl$, and on methylating this again, and then treating the new salt with silver oxide, trimethylamine and water are eliminated, and a new, vitreous, unsaturated *base*, which forms a *hydrochloride*, $C_{29}H_{25}O_4NMe_2,HCl$, is obtained.

Emetine is oxidised by alcoholic iodine at 100° to form *dehydroemetine iodide*, $C_{29}H_{32}O_4N_2I$, which crystallises in golden-yellow clusters, m. p. 177—179°, and is unaffected by alkali hydroxides. The halogen is removed by means of silver iodide, however, with the formation of an amorphous, yellow substance, m. p. 110°.

J. C. W.

Cephaeline Ethyl Ether. J. W. MEADER (Eng. Pat., 11718; from *J. Soc. Chem. Ind.*, 1916, **35**, 978—979).—*Cephaeline ethyl ether*, probably $C_{28}H_{37}O_3N_2{\cdot}OEt$, is obtained as a varnish-like substance by the action of ethyl bromide and an alcoholic solution of sodium ethoxide on cephaeline. It forms a crystalline *hydrochloride* (needles) and *hydrobromide*. The ether and its salts are valuable medicinal products. H. W.

***N*-Demethylocodeine (Norcodeine). II.** OTTO DIELS and ERNST FISCHER (*Ber.*, 1916, **94**, 1721—1724. Compare A., 1914, i, 989).—When codeineoxidesulphonic acid is oxidised with potassium chromate, it yields a compound, which Freund and Speyer (A., 1911, i, 909) designated "codeineoxidesulphonic acid hydrate," to which they assigned a formula with the same number of carbon atoms as the parent substance, thus: $C_{18}H_{21}O_7NS \longrightarrow C_{18}H_{23}O_8NS$. Formaldehyde is liberated during the oxidation, however, and the compound is really *norcodeinesulphonic acid*, $C_{17}H_{19}O_6NS$, whilst the base which Freund and Speyer obtained by heating it with water under pressure is norcodeine The acid decomposes at about 335°.

The elimination of the *N*-methyl group as formaldehyde also takes place when codeine oxide itself is heated with potassium chromate solution. J. C. W.

Preparation of Derivatives (Esters) of 4-Hydroxypiperidine and its *N*-Alkyl Derivatives. B. Emmert (D.R.-P., 292846; from *J. Soc. Chem. Ind.*, 1916, **35**, 1082).—Esters of 4-hydroxypiperidine and its *N*-alkyl derivatives with organic acids are prepared by the usual methods, and are valuable as local anæsthetics and as mydriatics. Examples mentioned are the benzoic and *p*-toluic esters of 4-hydroxypiperidine and the *o*- and *p*-toluic and *p*-nitrobenzoic esters of 4-hydroxy-1-methylpiperidine. H. W.

Catalytic Hydrogenations. XII. Hydrogenation of Heterocyclic Compounds. A. Skita and W. Brunner (*Ber.*, 1916, **49**, 1597—1605).—The best conditions are described for hydrogenating various pyridine, quinoline, and cinchona bases as completely as possible. Colloidal platinum, protected by gum arabic, is the catalyst employed.

Pyridine is quickly reduced in dilute hydrochloric acid solution to piperidine, and even to pentane and ammonia if the action is prolonged at 50°. α-Picoline reacts much more slowly, but yields in acetic acid solution α-pipecoline, and the velocity of the hydrogenation again diminishes rapidly in the cases of αγ-lutidine, which forms αγ-lupetidine, b. p. 140—142°, and collidine, which gives copellidine, b. p. 151—153°; hydrochloride, m. p. 287° (corr.), *platinichloride*, $C_8H_{17}N,H_2PtCl_6$, m. p. 248—249° (corr.). It is very necessary to use pure bases, isolated from the recrystallised picrates, to obtain good results, and the reduction is expedited by warming the solutions at 45—50°, chiefly owing to the increased solubility.

1-Phenylquinoline-3-carboxylic acid (atophan) may be reduced in warm solutions to 1-*phenyl*-1:2:3:4-*tetrahydroquinoline*-3-*carboxylic acid* (*tetrahydroatophan*), m. p. 218°, and finally to 1-*phenyldekahydroquinoline*-3-*carboxylic acid*, $C_{16}H_{21}O_2N$, m. p. 330° (decomp.).

Quinine, or, better still, dihydroquinine, or dihydrocinchonidine, may be reduced to *hexahydrocinchonidine*, $C_{19}H_{28}ON_2$, white leaflets, m. p. 206° (corr.), $[\alpha]_D^{17}$ −81°, *hydrochloride*, m. p. 281—282° (decomp.), and finally to *dodekahydrocinchonidine*, $C_{19}H_{34}ON_2$, a hygroscopic base, m. p. 104°, $[\alpha]_D^{17}$ −51°. Cinchonine or dihydroquinidine likewise yields *hexahydrocinchonine*, $C_{19}H_{28}ON_2$, which crystallises in slender needles, m. p. 241° (corr.), $[\alpha]_D^{20}$ +170·19°, and forms a *hydrochloride*, m. p. 308° (corr.). The preparation obtained from dihydroquinidine has to be freed from another *product*, $C_{20}H_{30}ON_2,H_2O$, m. p. 83°, which is soluble in ether. J. C. W.

Chromo-isomerism of the Acridonium Salts. A. Hantzsch (*Ber.*, 1916, **49**, 2169—2179. Compare A., 1911, i, 673).—In view of the criticisms and tentative suggestions of Kehrmann with

regard to the constitution of acridonium salts, a more exact study of the inter-relationships of the sulphites of phenylmethylacridonium, $\left[C_6H_4<\begin{smallmatrix}CPh\\|\\NMe\end{smallmatrix}>C_6H_4\right]_2SO_3$, has been made. When freshly prepared, the sulphite is yellow, but this salt very quickly changes into a green *dihydrate*. This loses water in a desiccator and changes into the same brown salt as is obtained if phenylmethylacridol is treated with sulphur dioxide in a dry solvent. This brown salt or the green hydrate forms a brown *alcoholate*, 1EtOH, or a brown additive *compound*, with $0{\cdot}5CHCl_3$, when dissolved in alcohol or chloroform, whereby it is noticed that the solution is first of all green for a shorter or longer time. Solutions in tetrachloroethane remain green for a considerable time, but deposit a brown *compound*, with $1C_2H_2Cl_4$, on evaporation. Pentachloroethane gives also a brown *compound*, with $0{\cdot}5C_2HCl_5$, from a stable, green solution, but if the original brown sulphite is triturated with this solvent, and then the solvent is washed away by means of light petroleum, a green *compound*, with $\frac{1}{3}C_2HCl_5$, is left, which loses the combined solvent on further treatment with petroleum, finally leaving the green *sulphite*, $(C_{20}H_{16}N)_2SO_3$. All these brown salts yield a brown sulphite free from combined solvent if treated with methyl alcohol, the solutions being yellow for a few moments before they change to brown.

Acridonium salts therefore give yellow solutions in water, methyl alcohol (labile), acetonitrile, or nitrobenzene, etc., brown in other alcohols, and green in ethyl alcohol and chloroform (labile), tetra- or penta-chloroethane, and the corresponding solid sulphites are the labile yellow salt, the brown salt and its compounds with solvents, and the green salt and its hydrate, mentioned above.

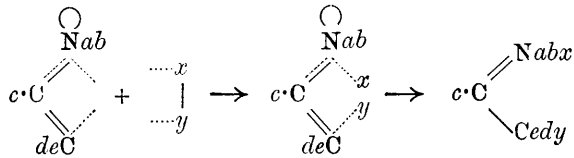
J. C. W.

An Extension of the Theory of Addition to Conjugated Unsaturated Systems. I. Constitution of the Salts of 1-Benzylidene-2-methyl-1:2:3:4-tetrahydro*iso*quinoline. ELLICE ETTIE PEDEN HAMILTON and ROBERT ROBINSON (T., 1916, **109**, 1029—1038).—1-Benzylidene-2-methyl-1:2:3:4-tetrahydro*iso*quinoline, prepared either by the dehydration of *N*-phenylacetyl-*β*-phenylethylmethylamine with phosphoric oxide in boiling xylene or by the action of an alkali hydroxide on the methochloride or methosulphate of 1-benzyl-3:4-dihydro*iso*quinoline, gives salts identical with the metho-salts derived from the latter substance. As the salts of the latter are almost certainly of normal structure, the formation of salts from the benzylidene base must be accompanied by a structural change of the type

$$C_6H_4<\begin{matrix}C(:CHPh)\cdot NMe\\ CH_2 \text{------} CH_2\end{matrix} \rightarrow C_6H_4<\begin{matrix}C(CH_2Ph):NMeI\\ CH_2 \text{------} CH_2\end{matrix};$$

similar reactions have already been observed (Decker, A., 1905, i, 667; Decker and Klauser, A., 1904, i, 338), for example, with *N*-methyl*iso*papaverine in salt formation. The authors regard

their observation as a strong confirmation of the existence of latent valencies in the conjugated $\cdot\dot{C}\colon\dot{C}\cdot\dot{N}\cdot$ nucleus and of the activity of these latent valencies in the reaction; they represent the processes of this type by the general scheme:



The two units of partial valency assumed for the tervalent nitrogen atom are regarded as quite distinct from the latent valencies which are capable of raising the atom to the quinquevalent condition, and these are represented in the above formulæ by the circular bond.

Piperonylidene-β-phenylethylamine,

$$CH_2\colon O_2\colon C_6H_3\cdot CH\colon N\cdot CH_2\cdot CH_2Ph,$$

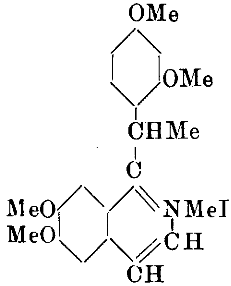
needles or prisms, m. p. 68—69°, obtained by the direct interaction of piperonal and β-phenylethylamine at the ordinary temperature, is readily resolved into its components by warm hydrochloric acid; in solution in methyl iodide at the ordinary temperature it undergoes gradual conversion into the corresponding *methiodide*, which slowly separates in flat, yellow needles; this substance is decomposed by warm water, giving rise to piperonal and *N*-methylphenylethylamine hydriodide (compare Forster, T., 1899, **75**, 936; Decker and Becker, A., 1913, i, 260). N-*Phenylacetyl-β-phenylethylmethylamine*, $CH_2Ph\cdot CH_2\cdot NMe\cdot CO\cdot CH_2Ph$, a colourless, viscid substance, b. p. 235°/20 mm., was prepared by treating an aqueous solution of phenylethylmethylamine with phenylacetyl chloride in the presence of free alkali.

1-*Benzylidene-2-methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*,

$$\begin{matrix} CH_2\cdot C_6H_4 \\ | \\ CH_2\cdot NMe \end{matrix}\!\!>\!C\colon CHPh,$$

a golden-yellow syrup, b. p. 213°/21 mm., is formed most conveniently by the action of cold potassium hydroxide solution on 1-benzyl-3 : 4-dihydro*iso*quinoline methochloride or methosulphate; it is also produced by the dehydration of *N*-phenylacetyl-β-phenylethylmethylamine in hot xylene solution with phosphoric oxide. The *hydriodide*, pale yellow, hexagonal tablets, m. p. 196—198° (decomp.), of the new base is obtained both when a solution of the base in sulphuric acid is treated with potassium iodide and when benzyldihydro*iso*quinoline is allowed to react additively with methyl iodide; the *aurichloride*, orange needles, m. p. 135—137°, is of the same characteristics whether prepared from the benzylidene base or from the methochloride of benzyldihydro*iso*quinoline; the *platinichloride*, orange-yellow prisms, m. p. 215—216°, is also obtainable from both bases. As explained above, these salts in structure are probably of the metho-salt type.

When *N*-methyl*iso*papaverine is heated with excess of methyl iodide for five hours, the product contains a methiodide of annexed constitution, as may be proved by conversion into the corresponding quaternary hydroxide and subsequent oxidation with permanganate to dimethoxy-*N*-methyl*iso*quinoline, and acetoveratrone [*salicylidene* derivative,



$$OH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}C_6H_3(OMe)_2,$$

bright yellow, prismatic needles, m. p. 153° with decomp.]. In the original alkylation, therefore, on account of the conjugated nitrogen–ethylene linking, the methyl radicle had become attached at a carbon atom.

In hot hydrochloric acid, the above salicylidene compound undergoes rapid conversion into 3′:4′-dimethoxy-2-phenyl-1:4-benzopyranol anhydroferrichloride,

$$\begin{matrix} C_6H_4{:}O(FeCl_4) \\ | \qquad\qquad \\ CH \text{———} CH \end{matrix} \!\!>\!\! C{\cdot}C_6H_3(OMe)_2,$$

chocolate-brown needles with green reflex, m. p. 201°. D. F. T.

[**Methylphenazonium Iodides.**] A. HANTZSCH (*Ber.*, 1916, **49**, 1865—1867).—Polemical. A reply to Kehrmann (this vol., i, 668). J. C. W.

Hydrazones of Diphenylenehydrazine. A. V. BLOM (*J. pr. Chem.*, 1916, [ii], **94**, 77—84).—The diphenylenehydrazones usually have higher melting points than the *as*-diphenylhydrazones, and some of them are sparingly soluble and crystallise readily. Further, diphenylenehydrazine is easily obtained pure, which is not the case with *as*-diphenylhydrazine.

Derivatives of carbazole with the substituents in the nucleus are readily converted into the corresponding hydrazines (compare Wieland, Süsser, and Fressel, A., 1912, i, 906), which yield well crystallisable hydrazones.

Diphenylenehydrazine [9-aminocarbazole] has m. p. 151° (Wieland, Süsser, and Fressel, *loc. cit.*, gave 147°) and dissolves in concentrated sulphuric acid, giving a colourless solution turned bright green by addition of a trace of nitric acid. For the preparation of the corresponding hydrazones the components must usually be heated together in absolute alcohol in presence of a little concentrated sulphuric acid or glacial acetic acid, although even under these conditions the hydrazones of certain ketones cannot be obtained. Most of these hydrazones dissolve readily, but those of ortho-substituted aldehydes are very slightly soluble. Methods of separation for mixtures of aldehydes and ketones may be based on these results.

Acetyldiphenylenehydrazine [*9-Acetylaminocarbazole*],

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} \!\!>\! N{\cdot}NHAc,$$

forms colourless needles, m. p. 247°, does not give Bülow's reaction, and dissolves in concentrated sulphuric acid with formation of a yellow coloration, which turns to green on addition of ferric chloride or alkali dichromate.

o-*Nitrobenzaldehydediphenylenehydrazone* [9-o-*nitrobenzylideneaminocarbazole*], $C_{19}H_{13}O_2N_3$, forms reddish-yellow needles, m. p. 149°, and is so slightly soluble in alcohol, even when warmed, that its formation serves for the detection of small proportions of 9-aminocarbazole. It undergoes no change when boiled with formaldehyde solution or when heated for several hours with anhydrous zinc chloride at 190°.

9-*Salicylideneaminocarbazole*, $C_{19}H_{14}ON_2$, forms colourless, silky needles, m. p. 147°, gives yellow solutions in various solvents, and dissolves in concentrated sulphuric acid to a golden-yellow liquid, which is not changed by addition of nitric acid.

9-o-*Methoxybenzylideneaminocarbazole*, $C_{20}H_{16}ON_2$, forms small, colourless needles, m. p. 147—148°, and dissolves in concentrated sulphuric acid to a golden-yellow solution, which is rendered paler by a little nitric acid and green by a few granules of dichromate.

9-m-*Hydroxybenzylideneaminocarbazole*, $C_{19}H_{14}ON_2$, forms thin, pale grey needles, m. p. 153—154°, with previous sintering, quickly darkens in the air, and is dissolved by concentrated sulphuric acid to an orange-yellow colour, which is scarcely altered by addition of a little nitric acid.

9-p-*Hydroxybenzylideneaminocarbazole* forms pale grey needles, m. p. 189°, and dissolves in concentrated sulphuric acid to a golden-yellow liquid, which is turned green by dichromate or ferric chloride and a transitory violet by a trace of nitric acid.

9-p-*Hydroxy*-m-*methoxybenzylideneaminocarbazole*, $C_{20}H_{16}O_2N_2$, forms slender, colourless needles, m. p. 129°, and gives a golden-yellow solution in concentrated sulphuric acid, which is turned dark green by a drop of nitric acid.

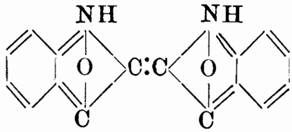
9-*Cinnamylideneaminocarbazole*, $C_{21}H_{16}N_2$, forms yellow needles or brownish-yellow prisms, m. p. 130—131°, and dissolves in concentrated sulphuric acid to a golden-yellow solution, which is turned pale yellowish-brown by a little nitric acid.

Acetophenonediphenylenehydrazone [9-*diphenylmethyleneaminocarbazole*], $C_{20}H_{16}N_2$, forms small, yellow crystals, m. p. 132°, and in concentrated sulphuric acid forms a golden-yellow solution, the colour of which is first destroyed and then gradually turned red by a trace of nitric acid. T. H. P.

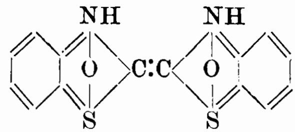
The Indigo Chromophore. M. CLAASZ (*Ber.*, 1916, **49**, 2079—2095).—It is customary to ascribe the tinctorial properties of indigotin to the grouping –CO·C:C·CO–, although attempts have been made to give a quinonoid configuration to the dye. Furthermore, the occurrence of this grouping in a compound has led Friedländer to adopt the description "indigoid," although some substances which do contain this system are not dyes, and others which resemble indigotin closely do not contain it. Such a dye is "thionylindigo" (A., 1912, i, 513) with the grouping –SO·C:C·SO–,

or more striking still, the sodium salt of the yellowish-red compound obtained by condensing isatin chloride with benzsulphonazoline (this vol., i, 425, 752). With these and other examples, the theory is developed that dyes of the indigo series are only formed when some auxochrome in the molecule so modifies the state of one benzene nucleus that a quinonoid configuration is acquired. This is rendered possible by the formation of a betaine-like ring, in which the carbonyl group participates.

Indigotin itself, therefore, is represented by the formula (I) and "thionylindigo" by (II). In the case of the compound derived



(I.)

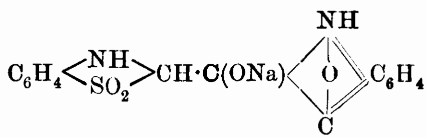


(II.)

from benzsulphonazoline and isatin chloride, the bridge-formation is hindered by the presence of the acidic $-SO_2-$ group, and the compound (III) has merely the yellowish-red colour due to the

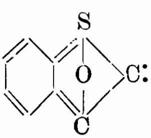
$$C_6H_4<\substack{NH \\ SO_2}>C:C<\substack{NH \\ CO}>C_6H_4 \rightarrow$$

(III.)



(IV.)

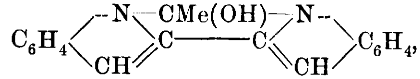
ethylene linking. Its sodium salt as an indigoid dye can be represented by formula (IV). This specific indigoid chromophore is not restricted to the imino-group as the auxochrome. Any electropositive auxochrome which can enter into inner-salt formation with a carbonyl group will give a similar chromophore (for example, the annexed one).



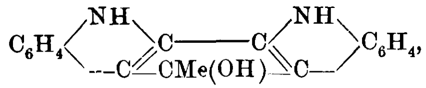
The above chromophore gives blue shades, whereas the sulphur compound gives reds, and in both cases the tints can be modified by the presence of the ethylene bridge as well. Numerous examples are discussed in the light of this theory. J. C. W.

New Derivatives of Di-indyl. W. MADELUNG and F. HAGER (*Ber.*, 1916, **49**, 2039—2050).—A C-acetyl, a N-acetyl, and a N:N-diacetyl derivative of di-indyl can be obtained under various conditions, but it is found to be impossible to acetylate the mono-derivatives further. This can only be explained by assuming that in these compounds the 1:1′-nitrogen atoms or the 3:3′-carbon atoms as the case may be are bridged across. There are many other indications that di-indyl exhibits a great tendency to form new ring systems in this way, one of which has already been mentioned in the case of 3:3′-imino-2:2′-di-indyl (A., 1914, i, 738).

The three acetyl derivatives are formed together when a concentrated solution of di-indyl in acetic anhydride is kept at 40—50°, and they can be separated by crystallisation. 1 : 1′-*Diacetyl*-2 : 2′-*di-indyl*, $C_{20}H_{16}O_2N_2$, forms readily soluble needles, m. p. 208°, whilst the N-*acetyl* compound, 1 : 1′-cyclo*acetyl*-2 : 2′-*di-indyl*,

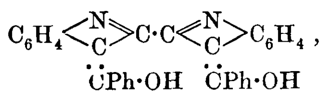


crystallises in sparingly soluble tablets or prisms, m. p. 212°. The C-*acetyl* compound, 3 : 3′-cyclo*acetyl*-2 : 2′-*di-indyl*,



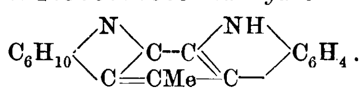
preponderates if di-indyl is boiled with acetic anhydride, and is also formed when acetyl chloride is added to an ethereal suspension of magnesium di-indyl bromide, which is obtained by mixing di-indyl with magnesium ethyl bromide in ether. The compound crystallises from acetic anhydride in long, glistening needles, m. p. 217°.

In contrast with the above, benzoyl chloride yields 3 : 3′-*dibenzoyl*-2 : 2′-*di-indyl*, m. p. 267°, either by direct application or through the intervention of the Grignard compound. This behaves as a di-enol of the formula



for it yields a *dipotassium* salt, pale yellow, rhombic tablets, almost insoluble in water, from which a *dimethyl ether*, m. p. 290°, and a *diethyl ether*, m. p. 258°, may be obtained by the action of the alkyl iodides.

Many attempts have been made to reduce di-indyl, but without much success. Treatment with concentrated hydriodic acid and acetic acid at 125° gives a compound which is a monacid base, and only forms additive compounds with acyl chlorides, and in which the 3 : 3′-carbon atoms are apparently united through the participation of the acetic acid. The product is therefore presumed to be 3 : 3′-cyclo*ethylidene*-4 : 5 : 6 : 7 : 8 : 9-*hexahydro*-2 : 2′-*di-indyl*,



It crystallises in colourless tablets, m. p. 214°, forms a *hydrochloride*, stout, dark brown needles, a *di-picrate*, brown needles, m. p. 165°, and yellow *additive* compounds with acetyl and benzoyl chlorides. J. C. W.

Heterocyclic Sulphones. V. "Sulphurylindigo" and "Sulphurylisatin." M. CLAASZ (*Ber.*, 1916, **49**, 1880—1883).—In a recent paper, a "trisulphurylisatodinitrile" was described as the product of the action of nitrous fumes on "sulphurylindoxyl"

(benzsulphonazoline) (this vol., i, 425). If the action is continued in hot solutions, the result is the oxidation of the methylene group to carbonyl or the oxidative linking of two molecules, with, therefore, the formation of an isatin and an indigotin. The "*sulphurylisatin*" (*benzsulphonazolone*), $C_6H_4<\begin{matrix}NH\\SO_2\end{matrix}>CO$, is the sole product if anhydrous solvents are used, or if the compound is nitrated and the moist nitro-derivative (*ibid.*) is at once added to sodium hydroxide. It is a brown powder, m. p. 150—155°, which dissolves in ammonia to give pure yellow or brown solutions, without the red tinge of ordinary isatin. The "*sulphurylindigo*,"

$$C_6H_4<\begin{matrix}NH\\SO_2\end{matrix}>C{:}C<\begin{matrix}NH\\SO_2\end{matrix}>C_6H_4,$$

is best obtained by oxidising with chromic acid in acetic acid solutions. It is a brown, microcrystalline powder, m. p. 106—110°, devoid of tinctorial properties.

Similarly, bromobenzsulphonazoline (*ibid.*) may be oxidised to "*αα'-dibromosulphurylindigo*,"

$$C_6H_4<\begin{matrix}NH\\SO_2\end{matrix}>CBr{\cdot}CBr<\begin{matrix}NH\\SO_2\end{matrix}>C_6H_4,$$

an ochre-coloured powder, m. p. 142—143°. J. C. W.

Formation and Properties of Compounds from 1 : 2-Diketones and Benzamidine. I. Diacetyl and Benzamidine. OTTO DIELS and KARL SCHLEICH (*Ber.*, 1916, **49**, 1711—1721).—Diacetyl combines with benzamidine when added to an aqueous solution of the hydrochloride mixed with sodium acetate, to form the *hydrochloride* of the *compound* $CPh\begin{matrix}\nearrow NH{\cdot}CMe{\cdot}OH\\ \qquad\quad | \\ \searrow N{-}{-}{-}CMe{\cdot}OH\end{matrix}$, which separates in fine crystals, m. p. 165°, and is readily decomposed into its parent substances on warming with water. A good method for purifying diacetyl is thus indicated. The compound condenses with benzaldehyde in alkaline solutions, yielding the *compound*

$$CPh\begin{matrix}\nearrow NH{\cdot}CMe{\cdot}O\searrow\\ \qquad | \\ \searrow N{-}{-}{-}CMe{\cdot}O\nearrow\end{matrix}CHPh,$$

in white crystals, m. p. 175°. When boiled with dilute hydrochloric acid the substance loses the elements of water, forming the *compound* $CPh\begin{matrix}\nearrow N{:}CMe\\ \quad | \\ \searrow N{\cdot}CMe{\cdot}OH\end{matrix}$, which crystallises in stout prisms, m. p. 202—203° (evolution of formaldehyde), and forms a *hydrochloride*, silky needles, m. p. 167—168° (decomp.) and other salts. This glyoxaline base condenses with phenylcarbimide to form the *compound* $C_{18}H_{17}O_2N_3$, short columns, m. p. 227°, and reacts with acetic anhydride in the cold to give the *acetyl* derivative, $C_{13}H_{14}O_2N_2$, m. p. 133°, which decomposes at 140—160° into a yellow substance. With boiling acetic anhydride, however, the base yields the colourless *compound*

$$\begin{matrix}CPh{:}N\\ | \\ N{:}CMe\end{matrix}>C<\begin{matrix}CH_2\\CH_2\end{matrix}>C<\begin{matrix}N{=}{=}CPh\\ | \\ CMe{:}N\end{matrix},$$

which crystallises with 2EtOH and has m. p. 222°. The base also loses the elements of formaldehyde when heated with ethyl malonate, forming *2-phenyl-4-methylglyoxaline*, $CPh\lessdot\begin{matrix}N—CMe\\ NH\cdot CH\end{matrix}$, in bundles of small needles, m. p. 293°. Nitric acid oxidises the base to the *compound* $C_{11}H_{12}O_2N_2$, long needles, which loses water at 108° and changes into the *compound* $C_{11}H_{10}ON_2$, m. p. 160°, bundles of long platelets. These give yellow solutions in water or alkalis, and the latter forms an *aniline* salt, yellow needles, m. p. 115—116°, which loses water at 80° in a vacuum and yields an *anilide*, $C_{17}H_{15}N_3$, m. p. 175°. The compounds are therefore regarded as hydroxymethylene derivatives, thus:

$$CPh\lessdot\begin{matrix}N:CMe\\ N\cdot C(OH)\cdot CH_2\cdot OH\end{matrix} \quad \text{and} \quad CPh\lessdot\begin{matrix}N:CMe\\ N\cdot C:CH\cdot OH\end{matrix}.$$

J. C. W.

Preparation of Barbituric Acid Derivatives. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 293163; from *J. Soc. Chem. Ind.*, 1916, **35**, 980).—Unsymmetrical disubstituted malonic acids of the general formula $CR^1R^2(CO_2H)_2$, where R^1 is an alkyl or aryl group and R^2 is an alicyclic radicle or a secondary alkyl group of the *iso*propyl type, are converted into barbituric acid derivatives by the usual methods, or the second substituent may be introduced into a mono-substituted barbituric acid prepared from the corresponding malonic acid derivative or from barbituric acid, or into one of the intermediate products obtained in the preparation of barbituric acid derivatives. Barbituric acid derivatives in which the carbon atom in the 5-position is attached to an alkyl or aryl group and to an alicyclic radicle or an *iso*propyl or similar secondary alkyl group are less toxic and have a more powerful hypnotic action than other symmetrical and unsymmetrical disubstituted barbituric acids. H. W.

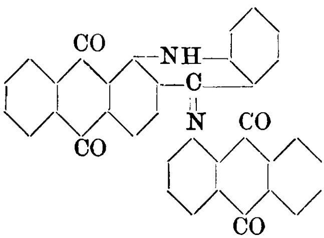
Action of *o*-Chlorobenzaldehyde on 1-Aminoanthraquinone. GEORG KALISCHER and FRITZ MAYER (*Ber.*, 1916, **49**, 1994—2000). —In D.R.-P., 280711, Cassella & Co. have described the preparation of a dye by heating together *o*-chlorobenzaldehyde and 1-aminoanthraquinone in the presence of an acid-fixing material and a little copper. The *dye*, $C_{42}H_{22}O_4N_2$ (2 mols. base + 2 mols. aldehyde − 2HCl − $2H_2O$), is a blue powder which dyes cotton bluish-green from a violet-red vat, and is formed, for example, when 1-aminoanthraquinone (10 parts), *o*-chlorobenzaldehyde (8), naphthalene (20), anhydrous potassium acetate (10), and cuprous chloride (0·4) are heated together for some hours at 225—230°.

This dye is not the only product of the interaction of the two agents. If they are heated together (1 mol. amine to 3 mols. aldehyde) with anhydrous sodium carbonate and a little copper powder in boiling nitrobenzene, they yield o-1-*anthraquinonyl*-

aminobenzaldehyde (1-o-*aldehydoanilinoanthraquinone*),

$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_3\cdot NH\cdot C_6H_4\cdot CHO,$$

in red crystals, m. p. 254°, which dye cotton pale bluish-violet from a reddish-violet hyposulphite vat. If the proportions of amine to aldehyde are 2 : 1, then the product of a similar treatment is 1-*anthraquinonyliminoanthraquinone*-2 : 1-*acridone* (5 - 1′ - *anthraquinonylimino*-1 : 2-*phthaloylacridine*) (annexed formula), which



crystallises in dark violet needles, and gives on heating a sublimate of 1-aminoanthraquinone and a residue of the above patented dye. It also decomposes into 1-aminoanthraquinone and anthraquinone-2 : 1-acridone (1 : 2-phthaloylacridine) on boiling with glacial acetic acid and concentrated hydrochloric acids. That the compound is formed by the oxidation of a condensation product of the above aldehyde, m. p. 254°, with 1-aminoanthraquinone is shown by the fact that it is also produced when *o*-chlorobenzaldehyde and 1-aminoanthraquinone are boiled with mercuric sulphate in nitrobenzene.

The aldehyde, m. p. 254°, will also condense with other amines to give substances which yield acridones on oxidation. Thus, when heated with aniline and mercuric sulphate in nitrobenzene, it forms *phenyliminoanthraquinone*-2 : 1-*acridone* (5-*phenylimino*-1 : 2-*phthaloylacridine*), which separates in coppery crystals and dyes cotton blue. This may also be obtained by heating anthraquinone-2 : 1-acridone (1 : 2-phthaloylacridine) with phosphorus pentachloride and condensing the dichloro-derivative so formed with aniline. J. C. W.

Preparation of Alkyl Esters of 1-Aryl-4-diethylaminoethyl-5-pyrazolone-3-carboxylic Acid. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 293287; from *J. Soc. Chem. Ind.*, 1916, **35**, 1083).—The previously unknown *alkyl esters* of 1-aryl-4-diethylaminoethyl-5-pyrazolone-3-carboxylic acid,

$$NEt_2\cdot[CH_2]_2\cdot CH{<}\genfrac{}{}{0pt}{}{C(CO_2R){:}N}{CO\text{———}N\cdot aryl},$$

have been found to possess pronounced anæsthetic properties. They are obtained by treating the esters of 1-aryl-5-pyrazolone-3-carboxylic acid, preferably in the form of their alkali salts, with halogenethyldiethylamines. H. W.

Triazoles from Dibenzamide or Di-*p*-toluamide and Hydrazine Salts. HERBERT WOLCHOWE (*Monatsh.*, 1916, **37**, 473—487).—Brunner has shown that aliphatic secondary amides react with semicarbazide or phenylhydrazine salts to form triazoles, even in

aqueous solutions (A., 1915, i, 1007). This reaction has now been extended to aromatic diamides, but, as might be expected, these react more sluggishly, and it is, indeed, necessary to fuse them with the hydrazine salts in order to obtain any quantity of the triazole. This procedure recalls Pellizzari's reaction, in which amides are distilled with hydrazides to form triazoles (A., 1911, i, 1035), and it might be supposed that in the case, for example, of the fusion of dibenzamide with phenylhydrazine hydrochloride, benzamide and benzoylphenylhydrazine are first formed and then react to form the triazole. It is shown, however, that at the temperature of the fused mixture, 150—160°, benzamide and benzoylphenylhydrazine do not react to any appreciable extent.

Dibenzamide, when fused with semicarbazide hydrochloride, yields 3 : 5-diphenyl-1 : 2 : 4-triazole, m. p. 190—191°; *acetyl* compound, m. p. 107—108°; *silver* salts, $C_{14}H_{10}N_3Ag$, decomp. 246°, and $C_{14}H_{10}N_3Ag,C_{14}H_{11}N_3$, decomp. 190—200° (compare Pinner, A., 1894, i, 385). With phenylhydrazine hydrochloride, it yields 1 : 3 : 5-triphenyl-1 : 2 : 4-triazole, and with β-naphthylhydrazine hydrochloride, 3 : 5-diphenyl-1-β-naphthyl-1 : 2 : 4-triazole (Engelhardt, A., 1897, i, 127). 3 : 5-*Diphenyl*-1-α-*naphthyl*-1 : 2 : 4-*triazole* is a pale grey powder, m. p. 131—132°, and 3 : 5-*diphenyl*-1-o-*tolyl*-1 : 2 : 4-*triazole* crystallises in rosettes of microscopic prisms or needles, m. p. 87—88°, and forms a *hydrochloride*, m. p. 178°. *p*-Tolylhydrazine hydrochloride yields the isomeric diphenyl-*p*-tolyl triazole, which forms a *hydrochloride*, m. p. 172° (Walther and Krumbiegel, A., 1903, i, 661).

Di-*p*-toluamide yields with phenylhydrazine hydrochloride 1-phenyl-3 : 5-di-*p*-tolyl-1 : 2 : 4-triazole (Engelhardt), and with semicarbazide hydrochloride, 3 : 5-di-*p*-tolyl-1 : 2 : 4-triazole (Pinner, A., 1895, i, 138). J. C. W.

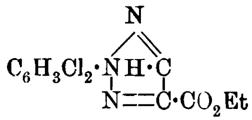
Action of Potassium Cyanide on the 2 : 4-Dichlorophenylhydrazone of Oxal-ester-chloride [Carbethoxyformyl Chloride]. (Transformation of Aceto- into Cyano-acetic Ester Derivatives.) CARL BÜLOW and PETER NEBER (*Ber.*, 1916, **49**, 2179—2203).—Ethyl sodiocyanoacetate condenses with neutral diazonium salts to form compounds which are usually met with in a labile, "α"-, and a stable, "β"-, modification, both of which form the same potassium salt. The constitution of these isomerides has engaged the attention of chemists from time to time, and the view is usually held that the stable ones are true hydrazones, thus,

$$R\cdot NH\cdot N:C(CN)\cdot CO_2R,$$

whilst the labile ones are the tautomeric azo-compounds or possibly cyclic structures of the type $NH:C\less\genfrac{}{}{0pt}{}{C(CO_2Et}{NR\text{———}}\gg N$, or that they may be stereoisomerides, Hantzsch being inclined to the last view (A., 1905, i, 615).

It is now found that the 2 : 4-dichlorophenylhydrazone of the ester chloride of oxalic acid, $C_6H_3Cl_2\cdot NH\cdot N:CCl\cdot CO_2Et$, reacts with potassium cyanide to give what can only be regarded as the true 2 : 4-dichlorophenylhydrazone of ethyl cyanoglyoxylate,

$C_6H_3Cl_2 \cdot NH \cdot N \colon C(CN) \cdot CO_2Et$, which is also formed when ethyl cyanoacetate is coupled with diazotised 2 : 4-dichloroaniline. This is yellow, and forms a yellow potassium salt, from which an excess of a mineral acid liberates a labile, white modification. Both isomerides yield an indifferent, white methyl derivative, which can be reduced to 2 : 4-dichloromethylaniline. In each case, therefore, the reactive hydrogen atom is attached to the nitrogen atom next to the benzene residue, which disposes of the azo-structure and the above cyclic formulation for the labile compound. The latter is supposed to be formed from the stable isomeride by the alternate addition and elimination of the elements of the mineral acid, resulting in the production of the annexed structure, which would explain the lack of colour and the chemical behaviour of the compound.

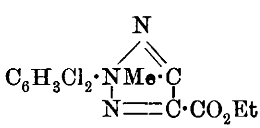


The 2 : 4-dichlorophenylhydrazone of oxalester-chloride is mixed with potassium cyanide in alcoholic solution, when the 2 : 4-*dichlorophenylhydrazone* of *ethyl cyanoglyoxylate* separates in golden-yellow needles, m. p. 177°, together with the product of the elimination of two molecules of hydrogen chloride from two of the starting material, namely, ethyl di-2 : 4-dichlorophenyldihydrotetrazinedicarboxylate,

$$CO_2Et \cdot C {<}{\begin{matrix} N \cdot N(C_6H_3Cl_2) \\ N(C_6H_3Cl_2) \cdot N \end{matrix}}{>} C \cdot CO_2Et,$$

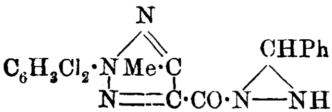
a representative of a class of compounds examined by Bowack and Lapworth (T., 1905, **87**, 1856). The pale lemon-yellow, labile *modification*, m. p. 103—104°, is obtained by carefully diazotising a suspension of 2 : 4-dichloroaniline hydrochloride in concentrated hydrochloric acid and adding the filtered solution to a mixture of sodium acetate and a dilute, alcoholic solution of ethyl cyanoacetate. The stable form is recovered unchanged from solution in concentrated sulphuric acid on dilution, or by the action of carbon dioxide on the yellow solution in potassium hydroxide, but if the solution of the potassium salt is added to a large excess of 10% hydrochloric acid, the labile modification is produced. This changes on melting, or on boiling with alcohol or glacial acetic acid for half an hour or so, into the stable form.

If the potassium salt is made into a paste with methyl sulphate and then warmed, the 2 : 4-*dichlorophenyl-α-methylhydrazone* is obtained, in rosettes of stout, white needles, m. p. 80°. On account of the lack of colour, the compound is regarded as conforming to the α-modification (annexed formula).



Unlike the hydrazone, with what is termed a "rolling, living" hydrogen atom, this methyl compound is easily hydrolysed to the carboxylic acid. The presence of an ester grouping is proved by the formation of the colourless *hydrazide*, $C_{10}H_9ON_5Cl_2$, m. p. 172°, which dissolves in acids or alkalis, the potassium salt being yellow. That is, the imido-hydrogen in the group $-CO \cdot NH \cdot NH_2$ is acidic,

and when this participates in the salt formation the molecule conforms to the open type of the stable hydrazone. Otherwise, the compound has the cyclic structure of the labile hydrazone. The presence of the amino-group in the hydrazide is demonstrated by the formation of a *benzylidene* compound, in white filaments, m. p. 205°. Although the basic properties have been destroyed by this condensation, the compound does not dissolve in alkalis, that is, the acidic imido-hydrogen has disappeared too. This is explained by the annexed formula for the compound.

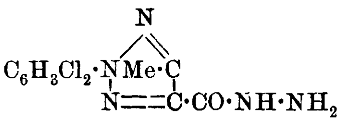


The above cyclic 2:4-dichlorophenyl-α-methylhydrazone of ethyl cyanoglyoxylate is reduced by zinc dust and hydrochloric acid (added drop by drop) to 2:4-*dichloromethylaniline*,

$C_6H_3Cl_2 \cdot NHMe$,

a white substance, m. p. about 40°, which forms an *acetyl* compound, prismatic tablets, m. p. 90°, a *nitroso*-compound, long, pale yellow needles, m. p. 54°, and a *platinichloride*, long, stout, orange-brown needles, m. p. 197—198°.

Starting with 2:5-dichloroaniline, a similar series of compounds has been obtained. The 2:5-*dichlorophenylhydrazone* of *ethyl cyanoglyoxylate* exists in the "open" form, in reddish-yellow leaflets, m. p. 146—147°, and in the cyclic form as pale yellow needles, m. p. 104·5°, which gives colourless solutions in most solvents with the exception of pyridine, which opens the ring. The cyclic 2:5-*dichlorophenyl-α-methylhydrazone* forms transparent, colourless, stout plates, m. p. 128—129°, and is converted by means of hydrazine hydrate into the cyclic *hydrazide* (annexed formula), which crystallises as a mass of white needles, m. p. 161—162°, and condenses with benzaldehyde to form the *benzylidene* compound, in bundles of limpid crystals, m. p. 197° (decomp.).



The phenylmethylhydrazone, m. p. 129°, on reduction, yields 2:5-*dichloromethylaniline*, an oil, which gives an *acetyl* compound, m. p. 69—70°, and a *nitroso*-compound, m. p. 66—67°. J. C. W.

Tetramethyldiaminophenazine. P. Karrer (*Ber.*, 1916, **49**, 1643—1644).—When a mixture of equimolecular quantities of dimethyl-*o*- and dimethyl-*m*-phenylenediamines, dissolved in hydrochloric acid, is oxidised by potassium dichromate, a small yield of *tetramethyl*-2:7-*diaminophenazine*, $NMe_2 \cdot C_6H_3 \lll{}^{N}_{N} \ggg C_6H_3 \cdot NMe_2$, is obtained. This is conveniently precipitated as the zincichloride in the presence of salt and then converted into the *hydriodide*, which is violet-red. J. C. W.

Aliphatic Diazo-compounds. III. H. Staudinger (*Ber.*, 1916, **49**, 1884—1897. Compare A., 1911, i, 751; 1912, i, 245).—In the main, an introduction to the following ten papers.

Many aliphatic diazo-compounds may be prepared by oxidising

the hydrazones of aldehydes or ketones with mercuric oxide. Most of them were obtained by Curtius in this way, but he regarded them as tetrazenes. Others have been prepared by an extension of von Pechmann's method, from nitrosourethanes. The so-called diazo-anhydrides have also been obtained by the action of acyl chlorides on ethyl diazoacetate, thus: $2N_2CH\cdot CO_2Et + R\cdot COCl = R\cdot CO\cdot CN_2\cdot CO_2Et + CH_2Cl\cdot CO_2Et + N_2$.

The colour of diazomethane is considerably deepened by the introduction of two radicles; thus the compound $CMe_2\colon N_2$ is red and $CPh_2\colon N_2$ bluish-red.

The stability of these diazo-compounds varies considerably. Some only lose nitrogen at 100° or above, and frequently the decomposition is attended by a violet luminescence, recalling "active" nitrogen. Tests for active nitrogen, according to Strutt, have, however, been negative. Many attempts have also been made to demonstrate the existence, if only in the nascent state, of substituted methylenes. Diazo-compounds have been decomposed in the presence of agents which should combine with methylenes, but only in the case of the decomposition of diazomethane in the presence of carbon monoxide has any trace of an expected product been obtained. These react to give keten, thus: $CH_2N_2 + CO = CH_2\colon CO + N_2$ (*loc. cit.*). What does happen when diazo-compounds are heated can be traced back to transformations of the methylene, however, and these fall into three classes (*loc. cit.*).

The constitution of diazo-compounds is discussed. An objection to the Thiele-Angeli formulation is that the introduction of one or two carbonyl groups at the methylene carbon atom diminishes the intensity of the colour and lowers the reactivity of the molecule, whereas in other cases in which carbonyl is placed adjacent to unsaturated groupings the colour and reactivity are enhanced (compare ketones and phenylhydrazones). Curtius's ring formulation still explains matters best, if it is assumed that the ring can easily be ruptured under appropriate treatment. J. C. W.

Aliphatic Diazo-compounds. IV. Comparison of the Nitrogen Scission in the Case of Different Aliphatic Diazo-compounds. H. STAUDINGER and ALICE GAULE (*Ber.*, 1916, **49**, 1897—1918).—The authors have made a gasometric study of the decomposition of diazo-compounds in cumene or bromobenzene solutions, under the influence of heat alone or in the cold in the presence of acetic acid or its chloro-derivatives. It is found that the catalytic influence of the acids increases with their strengths, but that few generalisations can be made with regard to the connexion between constitution, colour, and stability of the diazo-compounds. Very broadly speaking, it can be said that carbonyl groups diminish the intensity of the colour and increase the stability towards acids, but there seems to be no connexion between colour and the speed of decomposition by heat alone.

Many of the compounds examined are more particularly described in succeeding papers, but the chief factors of interest in the above connexion are summarised below.

Acetonehydrazone, conveniently obtained by heating ketazine with pure hydrazine, yields *dimethyldiazomethane* on shaking a cold solution in xylene with yellow mercuric oxide; a mobile, red liquid, b. p. $-31\cdot2°/14$ mm., with a stupefying odour, decomposes spontaneously, often with violence, at the ordinary temperature, very violently with acids. *Phenyldiazomethane*, from benzaldehydehydrazone, is a brownish-red liquid, b. p. 81°/15 mm., 37—43°/1·5 mm., with a "life" of a few days, and decomposes briskly in boiling xylene or with acids. Acetophenonehydrazone, m. p. 22°, yields *phenylmethyldiazomethane* as a dark red oil with a peculiar, sweet odour, which decomposes briskly within a few minutes at the ordinary temperature and yields with benzoic acid *α-phenylethyl benzoate*, CHMePh·OBz, a colourless oil, b. p. 170—172°/10 mm.

Diphenyldiazomethane, m. p. 29—30°, is deep bluish-red, keeps for a few days, decomposes briskly with boiling xylene, violently with glacial acetic acid; diphenylenediazomethane, m. p. 95°, is deep orange-red, keeps for months, fairly briskly decomposes in boiling xylene, violently with acetic acid; benzoylphenyldiazomethane, m. p. 79°, is orange-coloured, keeps for a few days, decomposes violently with boiling xylene or acetic acid; methyl diazoacetate, b. p. 33°/10 mm., is lemon-yellow, stable at the ordinary temperature, explodes on heating, decomposes slowly in boiling xylene, after a time with acetic acid and vigorously with dichloroacetic acid; ethyl diazoacetate, b. p. 46°/11 mm., is lemon-yellow, decomposes slowly with acetic acid, violently with dichloroacetic acid; diazoacetophenone, m. p. 50°, is pale yellow, stable at the ordinary temperature, slowly decomposed by boiling xylene or monochloroacetic acid, vigorously by dichloroacetic acid; dibenzoyldiazomethane, m. p. 114°, is very pale yellow, violently decomposes in boiling xylene; acetylbenzoyldiazomethane, m. p. 62°, is pale greenish-yellow, vigorously decomposed in boiling xylene or boiling dichloroacetic acid; diacetyldiazomethane, b. p. 57°/0·1 mm., is deep lemon-yellow, stable at the ordinary temperature, explodes on heating, violently decomposed in boiling xylene, moderately so in boiling dichloroacetic acid.

Methyl benzoyldiazoacetate is almost colourless, has m. p. 84°, is moderately briskly decomposed by boiling xylene, but may be recrystallised from boiling dichloroacetic acid; methyl acetyldiazoacetate is pale yellow, has b. p. 83°/12 mm., and decomposes very slowly in xylene or dichloroacetic acid on boiling; ethyl diazomalonate, b. p. 106—108°/10—11 mm., is pale yellow and very stable. J. C. W.

Aliphatic Diazo-compounds. V. Action of Hydrogen Sulphide on Diazo-compounds. H. STAUDINGER and J. SIEGWART (*Ber.*, 1916, **49**, 1918—1923).—The so-called diazo-anhydrides combine with hydrogen sulphide to form thiodiazoles, whereas most diazo-compounds hitherto examined were found to suffer reduction to hydrazones. For this reason, it has been assumed that the two classes of diazo-compounds are differently constituted. It is now

shown, however, that such a rigid distinction with regard to the reaction with hydrogen sulphide does not exist. Three main reactions are recognised: (1) those diazo-compounds in which the nitrogen ring is easily ruptured give thiols; (2) the proximity of carbonyl groups to the nitrogen ring strengthens this, and hydrogen sulphide may effect reduction to hydrazones, especially in the presence of ammonia; or (3) the carbonyl group may react with the hydrogen sulphide, and the ⌐CS group so formed undergo rearrangement with the nitrogen ring into a thiodiazole ring.

Diphenyldiazomethane reacts with hydrogen sulphide in alcoholic solution to give nitrogen and *thiobenzhydrol* (*diphenylmethylthiol*), which is a very unpleasant smelling, yellow oil, b. p. 128—130°/1·2 mm.

Benzoylphenyldiazomethane, suspended in alcohol, yields ethyl diphenylacetate, but in alcoholic ammonia the reaction is somewhat brisker, and diphenylacetamide is formed, mixed with *diphenylthiodiazole*, $\begin{matrix}\mathrm{CPh\cdot N} \\ \| \\ \mathrm{CPh{-}S}\end{matrix}\!\!>\!\mathrm{N}$, which is the main product when only a little ammonia is used. This compound forms white crystals, m. p. 93—94°, but soon becomes yellow in the light, and is decomposed by boiling in ethyl benzoate into tetraphenylthiophen, sulphur, and nitrogen. J. C. W.

Aliphatic Diazo-compounds. VI. Diphenyldiazomethane Derivatives. H. Staudinger and J. Goldstein (*Ber.*, 1916, **49**, 1923—1928).—The preparation and decomposition of some substituted diphenyldiazomethanes are described.

The *hydrazone* of *di*-p-*tolyl ketone*, m. p. 108—110°, when shaken with yellow mercuric oxide in benzene, yields *di*-p-*tolyldiazomethane*, $(C_6H_4Me)_2CN_2$, in permanganate-like crystals, m. p. 101°. This changes into the yellow *ketazine*, $N_2C_2(C_6H_4Me)_2$, m. p. 190—191°, on boiling with benzene or heating in a vacuum, and it also decomposes when left in carbon disulphide for a few days into *tetra*-p-*tolylethylene*, glistening, white crystals, m. p. 151°.

The *hydrazone* of *phenyl* p-*tolyl ketone*, m. p. 80—81°, yields *phenyltolyldiazomethane*, in violet-red needles, m. p. 53—55° (decomp.), which decompose spontaneously into the ketazine.

The *hydrazone* of *di*-p-*bromophenyl ketone*, small, white crystals, m. p. 92—94°, forms *di*-p-*bromophenyldiazomethane*, in pale red crystals, m. p. 90—92°, and this changes quickly in boiling benzene into the *ketazine*, $C_{26}H_{16}N_2Br_4$, m. p. 228—230°.

The *hydrazone* of *di-diphenylyl ketone*, m. p. 172°, condenses with benzaldehyde to form the *benzylidene* compound,

$$(C_6H_4Ph)_2C{:}N{\cdot}N{:}CHPh,$$

m. p. 69—70°, and is oxidised by mercuric oxide to the *ketazine*, $(C_6H_4Ph)_4C_2N_2$, m. p. 190°, the intermediate diazo-compound being too unstable to be isolated.

Curtius's 3-diazo-2-oxyindole (diazoisatin) (A., 1891, 451) decomposes when heated with benzene at 200° into 3:3-bis-indole (Wahl and Bayard, A., 1909, i, 330). J. C. W.

Aliphatic Diazo-compounds. VII. Diphenyldiazomethane. H. STAUDINGER, EUG. ANTHES, and F. PFENNINGER (*Ber.*, 1916, **49**, 1928—1941).—The preparation and reactions of diphenyldiazomethane are described. Although it is more deeply coloured than diazomethane, it is not so chemically active, whereas in the case of the ketens the coloured diphenylketen is more reactive than the colourless, unsubstituted keten.

Diphenyldiazomethane, $CPh_2{:}N_2$, is obtained in excellent yield by shaking a cold solution of benzophenonehydrazone in light petroleum with yellow mercuric oxide. It crystallises in dark Bordeaux-red needles, m. p. 29—30°, gradually decomposes into the ketazine, and explodes at about 115°, whereby a blue luminescence is observed at the moment before decomposition.

With boiling alcohol, it reacts slowly to form the ketazine and benzhydryl ethyl ether; with phenol, the reaction is rather violent, and the main product is apparently the benzhydryl phenyl ether. Carboxylic acids react briskly, but the action can be modified by dilution; benzoic acid gives a high yield of benzhydryl benzoate. Amines react very slowly in the cold; aniline at 100° yields diphenylmethylaniline.

Hydrogen chloride at −80° gives as the main product diphenylchloromethane, b. p. 168°/20 mm.; no indication of the formation of a diazonium chloride according to the scheme $CPh_2{:}N{:}N + HCl = CHPh_2{:}NCl{:}N$ being obtained.

When mixed with aniline and carbon disulphide, it forms *benzhydryl dithiocarbanilate*, $CHPh_2{\cdot}CS_2{\cdot}NHPh$, in colourless crystals, m. p. 129—130°.

Ethyl fumarate reacts with diphenyldiazomethane in ethereal solution to form *ethyl* 5 : 5-*diphenylpyrazoline*-3 : 4-*dicarboxylate*, $NH<\begin{matrix}CPh_2{\cdot}CH{\cdot}CO_2Et\\ N{=\!=}C{\cdot}CO_2Et\end{matrix}$, in colourless tablets, m. p. 137—138°, and this loses nitrogen at 190—200° and passes quantitatively into *ethyl* 1 : 1-*diphenyl*cyclo*propane*-2 : 3-*dicarboxylate*,

$$CPh_2<\begin{matrix}CH{\cdot}CO_2Et\\ CH{\cdot}CO_2Et\end{matrix},$$

m. p. 181°. Ethyl cinnamate, even undiluted, only discharges the colour of diphenyldiazomethane after about two months; on warming the syrup until the nitrogen evolution has ceased, *ethyl* 1 : 1 : 2-*triphenyl*cyclo*propane*-3-*carboxylate* may be obtained in colourless crystals, m. p. 93°. Diphenylketen and diphenyldiazomethane react together vigorously in ethereal solution to form, presumably, *tetraphenylpyrazolone*, $CO<\begin{matrix}CPh_2{\cdot}N\\ CPh_2{\cdot}N\end{matrix}$, in deep yellow crystals, m. p. 136°. This compound explodes mildly when heated, and leaves a brown resin which glows in the dark, even after some months if gently warmed.

When a solution of diphenyldiazomethane in light petroleum is left with carbonyl chloride, chlorodiphenylacetyl chloride is formed in excellent yield. Oxalyl chloride likewise forms chlorodiphenylpyruvyl chloride, but this, and the corresponding methyl ester,

decompose on heating, even in a high vacuum. The *anilide*, $CPh_2Cl\cdot CO\cdot CO\cdot NHPh$, however, crystallises with 1 mol. of benzene in white needles, m. p. 132—133°. Benzoyl chloride and ethyl chloroformate do not react with diphenyldiazomethane. Thionyl chloride reacts slowly, sulphuryl chloride violently, to form dichlorodiphenylmethane. J. C. W.

Aliphatic Diazo-compounds. VIII. Action of Sulphur Dioxide on Diphenyldiazomethane. H. STAUDINGER and F. PFENNINGER (*Ber.*, 1916, **49**, 1941—1951).—Diphenyldiazomethane reacts briskly with sulphur dioxide, but different products are obtained according to which of the agents is in excess. These can be explained, however, by the participation of the hoped-for product, diphenylsulphen, $CPh_2{:}SO_2$.

By adding a solution of diphenyldiazomethane to liquid sulphur dioxide, a high yield of benzophenone is obtained, which is explained by the scheme $CPh_2{:}SO_2 + SO_2 \longrightarrow CPh_2{<}\substack{SO_2\\ -O-}{>}SO \longrightarrow Ph_2CO + S_2O_3$ $(= S + SO_2)$. The existence of the oxide S_2O_3 could not be proved.

If, on the other hand, sulphur dioxide is led into a solution of diphenyldiazomethane in carbon disulphide, the ketazine, tetraphenylethylene, and *tetraphenylethylenesulphone* are formed, thus:

$$CPh_2{:}SO_2 + CPh_2{:}N_2 = \begin{matrix} CPh_2\cdot SO_2 \\ | \\ CPh_2-N \end{matrix}{\gg}N \longrightarrow$$

$$N_2 + SO_2{<}\begin{matrix} CPh_2 \\ | \\ CPh_2 \end{matrix} \longrightarrow C_2Ph_4 + SO_2.$$

This sulphone is white, but changes on crystallising from hot solvents such as benzene or carbon disulphide into a yellow *sulphone*, probably $C_6H_4{<}\substack{CHPh\\ CPh_2-}{>}SO_2$, which crystallises with $1CS_2$ in needles, m. p. 160°. A third *sulphone*, white crystals, m. p. 173—174° (decomp.), is obtained if the original sulphone is heated alone or shaken with methyl alcohol. These sulphones lose sulphur dioxide at 150—160° in a vacuum, and change into a colourless *hydrocarbon*, $C_{26}H_{20}$, m. p. 194—194·5°, isomeric with tetraphenylethylene.

If sulphur dioxide is led into alcoholic solutions of diphenyldiazomethane, the esters of *diphenylmethanesulphonic acid*, $CHPh_2\cdot SO_3H$, are formed. The acid is obtained from the esters by hydrolysis with aqueous alcohol; it crystallises from benzene with $1H_2O$, and has m. p. 111—112° (decomp.); the *methyl* ester has m. p. 101°, the *ethyl* ester, m. p. 71—72°. J. C. W.

Aliphatic Diazo-compounds. IX. Diphenylenediazomethane. H. STAUDINGER and ALICE GAULE (*Ber.*, 1916, **49**, 1951—1960).—Diphenylenediazomethane is conveniently prepared by the autoxidation of fluorenonehydrazone. For this purpose the hydrazone is suspended in alcohol containing a little dissolved sodium and shaken with glass beads, a current of purified air being admitted the while.

When left with dilute alcohol and a drop of hydrochloric acid the compound forms fluorenyl alcohol (Schmidt and Stützel, A., 1910, i, 29); with hydrogen chloride in ether it forms 9-chlorofluorene mixed with a little bi-diphenylene-ethylene; bromine gives 9 : 9-*di-bromofluorene*, colourless needles, m. p. 114°; aniline at 100° yields *fluorenylaniline*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>CH\cdot NHPh$, almost colourless needles, m. p. 121°; acetic acid produces fluorenyl acetate, m. p. 75°; benzoic acid yields much bi-diphenylene-ethylene and also a *fluorenyl benzoate*, m. p. 100°, isomeric with Schmidt and Stützel's ester, m. p. 161° (*ibid.*).

Ethyl fumarate reacts in ethereal solution to form *ethyl* 1-*di-phenylene*cyclo*propane*-2 : 3-*dicarboxylate*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C<\!\!\begin{matrix}CH\cdot CO_2Et\\|\\CH\cdot CO_2Et\end{matrix}$, in colourless crystals, m. p. 104°; the corresponding *acid* crystallises in tablets, which darken in colour at 270°. Similarly, ethyl cinnamate reacts in about three weeks to form *ethyl* 2-*phenyl*-1-*diphenylene*-cyclo*propane*-3-*carboxylate*, white leaflets, m. p. 116°, the corresponding *acid* forming pale orange crystals, m. p. 211°.

Diphenylketen also reacts slowly, yielding a *compound*, probably of the formula $N<\!\!\begin{matrix}N\text{---}C{:}C_{12}H_8\\|\\CPh_2\cdot CO\end{matrix}$, in yellow tablets which decompose at about 162°, giving nitrogen, but not carbon monoxide.

Carbonyl chloride gives rise to chlorodiphenyleneacetyl chloride, m. p. 129° (A., 1906, i, 861); oxalyl chloride yields *dichlorobi-diphenylenediacetyl* in colourless prisms, m. p. 190—191°, whilst oxalyl bromide gives the corresponding *compound*,

$$C_{12}H_8{:}CBr\cdot CO\cdot CO\cdot CBr{:}C_{12}H_8,$$

in yellow leaflets, m. p. 203—204°; sulphuryl chloride forms 9 : 9-dichlorofluorene. J. C. W.

Aliphatic Diazo-compounds. X. Attempts to Prepare Isomeric Diazo-compounds or Hydrazones. H. STAUDINGER and ALICE GAULE (*Ber.*, 1916, **49**, 1961—1968).—The formation of *cyclo*propane derivatives by the action of ethylenic compounds on diphenylenediazomethane (preceding abstract) suggested that azo-compounds might react in the same way to give substances of the type $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C<\!\!\begin{matrix}NR\\|\\NR\end{matrix}$. It was hoped that by a suitable choice, for example, a compound in which R represented an ester grouping, it might be possible to obtain the hydrazi-derivative, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C<\!\!\begin{matrix}NH\\|\\NH\end{matrix}$, and then the diazo-compound, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C<\!\!\begin{matrix}N\\||\\N\end{matrix}$. If this should differ from the original diphenylenediazomethane, the latter would conform to Thiele's formulation, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C{:}N{:}N$. It is found, however, that all hydrazi-compounds with free hydrogen undergo rearrange-

ment at once into hydrazones. If, therefore, compounds of the type $R_2C{<}\begin{matrix}NH\\|\\NH\end{matrix}$ seem to be incapable of existence and easily change into $R_2C{:}N{\cdot}NH_2$, it should not be difficult to assume that the azo-ring in $R_2C{<}\begin{matrix}N\\\|\\N\end{matrix}$ will also be easily ruptured under appropriate treatment. Müller's experience with hydrazi-compounds, prepared independently by the same method (A., 1915, i, 509) supports these views.

Diphenylenediazomethane reacts with ethyl azodicarboxylate to form *ethyl hydrazifluorenedicarboxylate*, $C_{12}H_8{:}C{<}\begin{matrix}N{\cdot}CO_2Et\\|\\N{\cdot}CO_2Et\end{matrix}$, in colourless prisms, m. p. 138—139°. This is hydrolysed by boiling concentrated hydrochloric acid to fluorenone and ethyl hydrazinedicarboxylate, and by sodium ethoxide to ethyl fluorenonehydrazonecarboxylate (see below). On heating at 150—180° it undergoes rearrangement into *ethyl fluorenonehydrazonedicarboxylate*,

$$C_{12}H_8{:}C{:}N{\cdot}N(CO_2Et)_2,$$

which forms pale yellow crystals, m. p. 116—117°, and is hydrolysed by boiling 0·5*N*-hydrochloric acid to benzophenone and ethyl hydrazinoformate, this being characterised by the production of ethyl benzaldehydehydrazonecarboxvlate, $CHPh{:}N{\cdot}NH{\cdot}CO_2Et$, on condensation with benzaldehyde. The ethyl ester is reduced by aluminium amalgam to an aluminium compound of fluorene, ammonia, and ethyl iminodicarboxylate, and is hydrolysed by sodium ethoxide in the cold to *ethyl fluorenonehydrazonecarboxylate*, $C_{12}H_8{:}C{:}N{\cdot}NH{\cdot}CO_2Et$, which crystallises in satin-like, greenish-white needles, m. p. 128—129°, and forms a yellow *sodium* salt which becomes red at 100°. J. C. W.

Aliphatic Diazo-compounds. XI. Reactions of Benzoylphenyldiazomethane. H. Staudinger (*Ber.*, 1916, **49**, 1969–1973).—If benzoylphenyldiazomethane (diazodeoxybenzoin) is treated with acid chlorides it might be expected to yield chlorobenzoylphenylacetyl chloride, which would serve as a source of benzoylphenylketen, thus:

$$N_2{\cdot}CPh{\cdot}COPh \longrightarrow CPhBzCl{\cdot}COCl \longrightarrow CPhBz{:}CO.$$

When left with carbonyl chloride for some weeks, it does yield the expected chloride, but this cannot be purified or converted into the keten. It is identified by conversion into *chlorobenzoylphenylacetanilide*, $C_{21}H_{16}O_2NCl$, m. p. 152—154°. At higher temperatures, diphenylketen or its compound with carbonyl chloride, diphenylmalonyl chloride, are formed.

Oxalyl chloride or bromide react vigorously, but give the tolan dihaloids, probably according to the scheme:

$$COPh{\cdot}CPhN_2 \longrightarrow CPhBzCl{\cdot}CO{\cdot}COCl \longrightarrow \begin{matrix}CPhCl-CPhCl\\|\qquad\quad|\\CO{\cdot}CO{\cdot}O\end{matrix} \longrightarrow$$

$$\begin{matrix}CPhCl{\cdot}CPhCl\\|\qquad\quad|\\CO\text{——}O\end{matrix} \longrightarrow CPhCl{:}CPhCl.$$

J. C. W.

Aliphatic Diazo-compounds. XII. Action of Acid Chlorides on [Benzene-substituted] Phenyldiazomethanecarboxylic Esters. H. STAUDINGER and CH. MÄCHLING (*Ber.*, 1916, **49**, 1973—1977).—Ethyl diazoacetate reacts with acyl chlorides to form new diazo-esters, whereas diphenyldiazomethane loses its nitrogen. The question was therefore raised: In which way does diazomethane or a carbonyl-substituted phenyldiazomethane react? In both cases nitrogen-free compounds are obtained (compare Clibbens and Nierenstein, T., 1915, **107**, 1491, for the diazomethane reactions).

o-Carbomethoxyphenyldiazomethane (methyl *o*-diazomethylbenzoate) (Oppé, A., 1913, i, 535) is a brick-red substance which keeps for a few days when dry. If distilled in a moist condition it yields some phthalide and *methyl* o-*methoxymethylbenzoate*,

$$OMe\cdot CH_2\cdot C_6H_4\cdot CO_2Me,$$

b. p. 124—125°/15 mm. With oxalyl chloride it reacts even at $-18°$ to form *ethyl chloro*-o-*carbomethoxyphenylpyruvate*,

$$CO_2Me\cdot C_6H_4\cdot CHCl\cdot CO\cdot CO_2Et,$$

m. p. 54—55°. Benzoyl bromide gives rise to *methyl* o-*α-bromo-α-benzoylmethylbenzoate*, $CO_2Me\cdot C_6H_4\cdot CHBrBz$, m. p. 78—79°, whilst benzoyl chloride gives an orange-yellow *compound*, $C_{18}H_{15}O_4Cl$, m. p. 79—80°. J. C. W.

Aliphatic Diazo-compounds. XIII. Action of Acid Chlorides on Ethyl Diazoacetate. H. STAUDINGER, J. BECKER, and H HIRZEL (*Ber.*, 1916, **49**, 1978—1994).—Practically all the acyl chlorides examined react with ethyl diazoacetate according to the scheme:

$$2CHN_2\cdot CO_2Et + R\cdot COCl = R\cdot CO\cdot CN_2\cdot CO_2Et + CH_2Cl\cdot CO_2Et.$$

Thus, carbonyl chloride yields ethyl chloroacetate and *diazocarbethoxyacetyl chloride*, $CO_2Et\cdot CN_2\cdot COCl$, a viscous, yellow oil, b. p. 63·5—64·5°/0·02 mm., which may be converted into the amide, pale yellow needles, m. p. 142°, and the *p*-toluidide, m. p. 95—96°, and also into ethyl diazomalonate, b. p. 106°/10 mm. (compare Neresheimer, *Diss.*, Munich, 1908).—Ethyl chloroformate is without action. At about 100°, however, carbonyl chloride reacts with the ester–chloride further, to give the compound, $CO_2Et\cdot CCl(COCl)_2$, which is characterised by the p-*toluidide*,

$$CO_2Et\cdot CCl(CO\cdot NH\cdot C_7H_7)_2,$$

m. p. 124—125°.

Acetyl chloride yields ethyl diazoacetoacetate (Wolff, A., 1903, i, 203); propionyl chloride gives *ethyl diazopropionoacetate*, $C_2H_5\cdot CO\cdot CN_2\cdot CO_2Et$, as a pale yellow, limpid oil, b. p. 58—59°/0·15 mm. Benzoyl bromide and methyl diazoacetate yield *methyl diazobenzoylacetate*, $N_2{:}CBz\cdot CO_2Me$, in pale yellow tablets, m. p. 83—84°, which are very stable towards acids, but easily suffer ester hydrolysis, but not ketone hydrolysis, when treated with alkalis. The same ester can be obtained by Wolff's method from methyl oximinobenzoylacetate. It may be condensed with aniline in glacial acetic acid to form methyl 1:5-diphenyl-1:2:3-triazole-4-carboxylate, $NPh<\begin{matrix}N{=}{=}N\\ CPh{:}\overset{|}{C}\cdot CO_2Me\end{matrix}$, which Dimroth ob-

tained from phenylazoimide and methyl benzoylacetate (A., 1903, i, 127). With methyl-alcoholic ammonium hydrogen sulphide, it yields *methyl* 5-*phenyl*-1 : 2 : 3-*thiodiazole*-4-*carboxylate*,

$$S<\begin{matrix}CPh\colon C\cdot CO_2Me\\ N{=\!=}N\end{matrix},$$

silky needles, m. p. 60°, the corresponding acid and ethyl ester having been obtained by Wolff (A., 1904, i, 828).

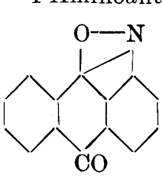
Cinnamoyl chloride reacts very sluggishly, but *cinnamoyl bromide* (long, yellow needles, m. p. 43°, b. p. 119—121°/0·2 mm.), forms *methyl diazocinnamoylacetate*, $CHPh\colon CH\cdot CO\cdot CN_2\cdot CO_2Me$, in pale yellow tablets, m. p. 115°, occasionally mixed with a more soluble *isomeride*, colourless crystals, m. p. 146—147°.

Carbethoxyformyl chloride (oxal–ester–chloride) forms *ethyl diazoketosuccinate*, $CO_2Et\cdot CO\cdot CN_2\cdot CO_2Et$, as a pale yellow, viscous oil, b. p. 96—100°/0·05 mm., whereas oxalyl chloride reacts more vigorously and gives the *ester–chloride*, $COCl\cdot CO\cdot CN_2\cdot CO_2Et$, as a pale yellow oil, b. p. 84—85°/0·01 mm., which is characterised by the p-*toluidide*, long, slender needles, m. p. 163—164° (decomp.). Oxalyl chloride and methyl diazoacetate react in cold ether to form *methyl bisdiazodiketoadipate*, $CO_2Me\cdot CN_2\cdot CO\cdot CO\cdot CN_2\cdot CO_2Me$, in pale yellow tablets, m. p. 96—97°. J. C. W.

Benzoyleneanthranil, Bisanthranils and Azoiminoanthraquinones. ALFRED SCHAARSCHMIDT [with ANDREE CONSTANDACHI and MAX THIELE] (*Ber.*, 1916, **49**, 1632—1637).—Anthraquinonediazonium salts react with sodium azide to form anthraquinonylazoimides. Those derivatives with the azoimide residues in position 1, 1 and 4, or 1 and 5 are very unstable, and undergo rearrangement into anthranil compounds on warming with water.

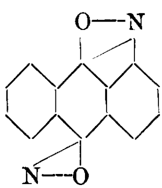
1-Aminoanthraquinone yields 1-*azoiminoanthraquinone*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3\cdot N_3,$$

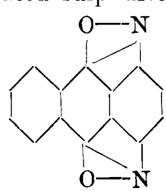


a yellow precipitate, and this forms 3 : 4-*benzoyleneanthranil* (annexed formula), yellow needles, m. p. above 300°, the evolution of nitrogen being quantitative.

1 : 5-Diaminoanthraquinone yields the yellow 1 : 5-*bisazoiminoanthraquinone*, and this forms a *bisanthranil* of the formula (I) in glistening, steel-blue needles, which exhibit intense yellowish-green fluorescence in concentrated sulphuric acid:



(I.)



(II.)

1 : 4-*Bisazoimidoanthraquinone* is red, and forms the iso*bisanthranil* derivative, (II), as a reddish-brown, crystalline powder.

5-*Chloro*-3 : 4-*benzoyleneanthranil*, m. p. 212°, is obtained from

4-chloro-1-aminoanthraquinone, and *7-bromo-3:4-benzoyleneanthranil*, m. p. 242°, from 2-bromo-1-aminoanthraquinone. Both compounds crystallise in pure yellow needles.

2-Azoiminoanthraquinone is stable, and crystallises in yellow needles, m. p. 160°. J. C. W.

Azoimino- and Stereoisomeric Azo- and Hydrazo-derivatives of Anthraquinone. L. GATTERMANN and R. EBERT (*Ber.*, 1916, **49**, 2117—2120).—When equimolecular proportions of hydroxylamine hydrochloride and 1-anthraquinonediazonium sulphate are mixed in concentrated solutions, *1-anthraquinoneazohydroxylamide*, $C_{14}H_7O_2\cdot N{:}N\cdot NH\cdot OH$, is deposited in pale red needles. This forms a double *compound* with pyridine (1 mol.), in large, red leaflets, and is transformed by treatment with acetic anhydride into 1-azoiminoanthraquinone, which loses nitrogen on boiling with xylene. Schaarschmidt (preceding abstract) obtained the same azoimide, and designated the decomposition product "benzoyleneanthranil"; but the present authors suggest the name "*semiazoanthraquinone*," and assign to it a formula with univalent nitrogen, thus, $C_6H_4{<}{}^{CO}_{CO}{>}C_6H_3\cdot N$. When this is heated in the dry state at about 170—200°, it changes into *1-azoanthraquinone*, $C_{28}H_{14}O_4N_2$, which exists in a yellow form, less soluble in nitrobenzene, and a red modification. These isomerides yield different hydrazo-compounds on reduction with phenylhydrazine or a hyposulphite. J. C. W.

Preparation of Dinitroalkylaminophenylarsinic Acids. C. F. BOEHRINGER & SÖHNE (D.R.-P., 292546. Addition to D.R.-P., 285604; from *J. Soc. Chem. Ind.*, 1916, **35**, 979).—Mononitroalkylaminophenylarsinic acids or their 2-halogen derivatives (British Pat., 1913, 29546; A., 1915, i, 32) are nitrated with the calculated quantity of nitric acid in presence of concentrated sulphuric acid. H. W.

Dyes Derived from Aminophenylarsinic Acid. E. NOELTING (*Bull. Soc. chim.*, 1916, [iv], **19**, 341—343).—The author has prepared a series of coloured derivatives from *p*-aminophenylarsinic acid by diazotising it and coupling it with β-naphthol and the β-naphtholsulphonic acids. All these compounds dye wool mordanted with iron, aluminium, or chrome mordants in an intense manner, the shades varying from orange-yellow to reddish-brown. The mordants which fix these colouring matters best are chromium, aluminium, iron, titanium, zirconium, thorium, yttrium, glucinum, tin, and bismuth. On the other hand, cobalt, nickel, copper, zinc, cadmium, manganese, lead, and antimony do not fix them at all. From the point of view of shade of colour, the derivatives of aminophenylarsinic acid are scarcely to be distinguished from those of sulphanilic or *p*-aminobenzoic acids. The derivatives of sulphanilic acid, however, possess no affinity for the mordants, those of aminobenzoic acid possess a slight affinity, and those of aminophenylarsinic acid a very marked affinity. W. G.

Aromatic Arsenic Compounds. XI. Mixed Arseno-compounds. P. KARRER (*Ber.*, 1916, **49**, 1648—1650).—When two symmetrical arseno-compounds are warmed together in solution, an exchange of groupings takes place very readily, thus: $R_2As_2 + R'_2As_2 = 2RAs:AsR'$. For example, solutions of the hydrochlorides of 3 : 4 : 5 : 3′ : 4′ : 5′-hexa-aminoarsenobenzene and 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene, warmed at 80° and then slowly poured into a large volume of hydrochloric acid (D 1·12), deposit 3 : 4 : 5 : *3′-tetra-amino-4′-hydroxyarsenobenzene hydrochloride*, $B,3HCl,3H_2O$, in yellow flocks, whilst the hexa-amine salt and 3 : 5 : 3′ : 5′-tetra-amino-4 : 4′-dimethyldiaminoarsenobenzene hydrochloride yield 3 : 4 : 5 : 3′ : *5′-penta-amino-4′-methylaminoarsenobenzene hydrochloride*, B,4HCl. J. C. W.

Physiological Chemistry.

Sugar of the Blood and in the Urine, in Varying Conditions of Health, in the Bengali. D. McCay (*Indian J. Med. Research*, 1916, **4**, 1—27).—In Bengalis the average percentage of blood sugar is 0·13, as compared with 0·08 in Europeans; the high content is probably due to an excessive carbohydrate diet. The poor working classes have an average of 0·125%, and in this energetic and lean type, administration of large amounts of sugar produces scarcely any increase in the blood sugar, the excess being probably all deposited in the liver as glycogen. The fat, indolent type of Bengali, with 0·15% blood sugar, on the other hand, has a low sugar tolerance. The glycogenic functions vary with the individual, as also the concentration of the blood sugar which is approximately constant for each person. G. B.

Changes in the Cholesterol Content of the Blood of Goats following Cholesterol Feeding Alone, Treatment with Röntgen Rays Alone, and Cholesterol Feeding Combined with Treatment with Röntgen Rays and Subsequent Castration. Georgine Luden (*J. Biol. Chem.*, 1916, **27**, 273—297).—The results are very indefinite, but it appears that feeding with cholesterol leads to an increase in the cholesterol content of the blood, whilst the treatment with Röntgen rays diminishes it. Castration also tends to increase the amount of cholesterol in the blood. H. W. B.

Influence of Ether Anæsthesia on Amino-acids of Blood serum. Ellison L. Ross (*J. Biol. Chem.*, 1916, **27**, 45—50).—There is a slight diminution of the amount of amino-acids in the blood of dogs after fifteen minutes' anæsthesia, which is most marked if the ether is administered at the time when the content of amino-acids in the blood is at its maximum about four hours after a protein meal. H. W. B.

The Factors Concerned in the Formation of Thrombin HENRY HALLETT DALE and GEORGE STANLEY WALPOLE (*Biochem. J.*, 1916, **10**, 331—362).—An account is given of experiments in which attempts are made to prepare the various factors involved in the coagulation of the blood in a state of physiological purity. The following were obtained: (*a*) Fibrinogen, which contained neither prothrombin nor kinase, was obtained from oxalated mammalian plasma by the method of Bordet and Delage by adsorbing the prothrombin by barium sulphate, and then precipitating the fibrinogen by half-saturation with sodium chloride. (*b*) Prothrombin was separated from a mixture of prothrombin and fibrinogen obtained from fowl's plasma by taking advantage of the fact that it is soluble in a weaker solution of sodium chloride than is fibrinogen. The method, which is described in detail, is a modification of that suggested by Mellanby. (*c*) The kinase was prepared from fowl's testes.

It was found that fresh fowl's plasma, when shaken with chloroform, yields a powerful thrombin; if previously treated with calcium, a mixture of prothrombin and kinase is obtained, which can often be obtained apart by centrifuging the chloroform from the watery residue. If the treatment with chloroform is continued for some days, a kinase is the only clotting factor remaining. A similar formation of kinase and (in the presence of calcium) thrombin occurs when fowl's plasma is treated with sufficient trypsin, and this seems to indicate that the action of chloroform is due to the liberation of the normal tryptic ferment by the destruction of antitrypsin. A large number of experiments have also been carried out to test Howell's theory, according to which prothrombin is associated with an antithrombin, which complex is dissociated by the action of the kinase. The results obtained by the authors fail to substantiate this theory.

S. B. S.

Anaphylaxis to the Separated Proteins of Horse-serum. HENRY HALLETT DALE and PERCIVAL HARTLEY (*Biochem. J.*, 1916, **10**, 408—433).—Each of the three proteins of horse-serum, euglobulin, ψ-globulin, and albumin, can act as an anaphylactic antigen, and a guinea-pig which has been sensitised to one of them is more sensitive to that than to any other from the same serum; in some cases even the sensitisation appears to be rigidly specific. The sensitiveness to the albumin fraction is of later development than that to the globulins in the case of guinea-pigs, and it is this fact, probably, which has caused other observers to miss the sensitising property of the albumin. The difference is specially marked when sensitisation is carried out with serum itself containing all three proteins. An effective dose of any of the proteins to which the plain muscle of the guinea-pig has been sensitised, partly or completely de-sensitises it to the other proteins of the same serum. The crystalline albumins from the egg-white of hens and ducks show no differences in their antigenic properties.

S. B. S.

Clinical Calorimetry. XVIII. The Number of Places of Significant Figures in the Data of Metabolism Experiments. FRANK C. GEPHART, EUGENE F. DU BOIS, and GRAHAM LUSK (*J. Biol. Chem.*, 1916, **27**, 217—223).—In experimental work on metabolism, the analytical error is seldom less than 1%. A variation of 1% in the result of an experiment does not change its significance or affect its interpretation. For these reasons, the authors point out that it is unnecessary to publish more than three significant figures in the tables of data, thereby saving printer's ink and facilitating recalculation of the work by other investigators. H. W. B.

Feeding Experiments with a Dietary in which Tyrosine is Reduced to a Minimum. GINZABURO TOTANI (*Biochem. J.*, 1916, **10**, 382—397).—Experiments are described in which attempts are made to separate completely tyrosine from digestion mixtures of caseinogen. The author has not been completely successful in this respect, but he describes a method by means of which nearly all may be removed. For this purpose, the protein is digested first with trypsin and afterwards hydrolysed with acids. The almost complete removal of tyrosine from the mixture of amino-acids thus obtained has practically no effect on its nutritive value when tested on young rats. In the case of gelatin, it is found that the hydrolysed product has greater nutrient value than when fed intact to rats, as in the latter case it is not well digested. It is possible to obtain a complete substitute for proteins in a diet by hydrolysed gelatin with the addition of certain amino-acids, and there is some evidence that the addition of tryptophan alone to these products will suffice. S. B. S.

Feeding Experiments with Kynurenic Acid. CHUAI ASAYAMA (*Biochem. J.*, 1916, **10**, 466—472).—Rats were fed on a basal diet containing all the necessary amino-acids except tryptophan. When tryptophan is added to the diet they maintain their normal weight. This is not the case, however, when tryptophan is replaced by kynurenic acid, which does not appear, therefore, to have any special significance in metabolism. S. B. S.

Relation of the Unidentified Dietary Factors, the Fat-soluble *A*, and Water-soluble *B*, of the Diet to the Growth-promoting Properties of Milk. E. V. MCCOLLUM, N. SIMMONDS, and W. PITZ (*J. Biol. Chem.*, 1916, **27**, 33—43. Compare McCollum and Davis, this vol., i, 184).—The authors have studied the effect on the growth of young rats of the withdrawal of the accessory factors designated fat-soluble *A* and water-soluble *B* from the diet of the mother. In all cases the young may continue to thrive for a short time at the expense of the tissues of the mother, but soon growth ceases, and is only resumed when the missing factors are added to the mother's diet. Apparently the maternal organism is unable to synthesise these substances which are essential for the well-being of the offspring. H. W. B.

Certain Dietary Conditions bearing on the Problem of Growth in Rats. CASIMIR FUNK and JOSEPH POKLOP (*J. Biol. Chem.*, 1916, **27**, 1—14. Compare this vol., i, 696).—Rats thrive and grow well on a diet of oats, bread, condensed milk, and yeast. An equivalent amount of milk may be substituted for the yeast, but the growth is not then so rapid. Orange juice cannot replace the yeast. Oats, in conjunction with sodium hydrogen carbonate or alone, is an inadequate food for young rats. H. W. B.

Nutritive Properties of Maize. ALBERT G. HOGAN (*J. Biol. Chem.*, 1916, **27**, 193—208).—Rats on a maize diet grow more rapidly when the grain is supplemented with salts than with additional protein. In the case of pigs, additional protein is more beneficial than additional salts. The author suggests that maize is deficient in vitamines, although they are present in sufficient amount to maintain normal growth in pigs. An adequate supplemented maize diet becomes inadequate after heating in an autoclave for a few hours at a high temperature. H. W. B.

Cotton-seed Meal as an Incomplete Food. C. A. WELLS and P. V. EWING (*J. Biol. Chem.*, 1916, **27**, 15—25).—The authors consider that the detrimental effect on the growth of the pig of the inclusion of cotton-seed meal in the diet is due largely to a deficiency of vitamines in the food. When this deficiency is removed by the addition of milk to the diet, the injurious action of the cotton-seed meal becomes relatively insignificant.

H. W. B.

Growth. III. Comparative Value of Lard and Butter Fat in Growth. CASIMIR FUNK and ARCHIBALD BRUCE MACALLUM (*J. Biol. Chem.*, 1916, **27**, 51—62. Compare this vol., i, 184).—The growth of rats is not maintained on a lard and dried yeast diet. Substitution of moist yeast for the dry material increases the efficiency of the diet, which can be still further improved by replacing the lard by butter. Even in the latter case, the existing deficiencies are not entirely corrected, since many rats decline on this diet. Rats which fail on lard do not always recover on a diet containing butter. It appears that yeast, probably on account of its high content of purines, is not an ideal addition in experiments of long duration, in spite of its marked growth-promoting power. H. W. B.

Growth. IV. Action of Yeast Fractions on the Growth of Rats. CASIMIR FUNK and ARCHIBALD BRUCE MACALLUM (*J. Biol. Chem.*, 1916, **27**, 63—70).—When extracts of yeast are treated with phosphotungstic acid the growth-promoting substance is carried down with the precipitate, and thereby a large part of its activity is lost. The subsequent removal of the purines by fractionation with silver salts is attended with almost complete loss of growth-promoting power. It appears that considerably larger quantities of vitamines are necessary for stimulating growth than

for curing beri-beri, and the substance or substances concerned in the former case are less stable and more easily destroyed during fractionation than those concerned in the latter. H. W. B.

Nutritive Value of Yeast, Polished Rice, and White Bread as Determined by Experiments on Man. CASIMIR FUNK, W. G. LYLE, and DONALD MCCASKEY, with JOSEPH CASPE and JOSEPH POKLOP (*J. Biol. Chem.*, 1916, **27**, 173—191).—Experiments on four men are described in which the chief source of protein in the diet for fourteen days was yeast, whilst in the following ten to fourteen days the diet consisted chiefly of rice and bread.

Yeast is badly absorbed and assimilated, and its high content of purines leads to a considerable rise of uric acid in the blood and urine. A large part of the yeast nitrogen is apparently unutilised, so that the amount of nitrogen which is fully adequate in the form of rice and bread to maintain nitrogenous equilibrium is insufficient when yeast is employed. In the cases described a positive nitrogen balance was seldom obtained even after the administration of an extra proportion of vitamine in the form of an extract of autolysed yeast. The authors hesitate to declare that yeast possesses no value in dietetics, but state that it cannot be recommended as a sole source of protein. H. W. B.

Isolation of a Growth-producing Substance from the Pancreas of the Sheep. WALTER H. EDDY (*J. Biol. Chem.*, 1916, **27**, 113—126).—The addition of the water-soluble portion of an alcoholic extract of pancreas to a diet which by itself is inadequate to maintain the life of rats is followed usually by marked growth of the animals. The growth-producing substance is not an amino-acid, but is precipitated by phosphotungstic acid, and can be removed from its aqueous solution without loss of activity by treatment with Lloyd's reagent (colloidal aluminium silicate).

H. W. B.

The Chemistry of the Vitamines. ROBERT R. WILLIAMS (*Philippine J. Sci.*, 1916, [A], **11**, 49—57. Compare this vol., i, 770).—Attempts were made to isolate vitamine as a pure chemical individual, but without success. A detailed description is given of the method employed for the isolation of a concentrated vitamine preparation from rice polishings. The method is essentially that used by Funk, and it yielded 0·2—0·25 gram of curative substance from 25 kilos. of polishings. The curative properties of the following synthetic products were also tested by feeding to neuritic fowls per os: Nicotinic acid, *p*-hydroxynicotinic acid, methyl nicotinate hydrochloride, and trigonelline. Little or but temporary improvement was observed in any of the cases. An inner condensation product of hydroxynicotinic acid prepared by the action of phosphoric oxide caused in 0·1 gram doses considerable improvement in two cases and an apparent cure in a third.

G. F. M.

The Pigmentary Composition of Hepatochlorophyll. CH. DHÉRÉ and G. VEGEZZI (*Compt. rend.*, 1916, **163**, 399—401).—The authors have isolated the different pigments contained in the hepatochlorophyll of the liver of *Helix pomatia*, by using Tsvett's method of chromatographic analysis by adsorption. This hepatochlorophyll has the same pigmentary composition as the "crude chlorophyll" obtained from green leaves. It consists of a mixture of α- and β-chlorophyllans, carotin, and xanthophyll. All these pigments were isolated in a state of optical purity, this being the first time that β-chlorophyllan has been found in the animal kingdom. The origin of the hepatochlorophyll is due to a chlorophyll introduced in the form of plant food (compare MacMunn, *Phil. Trans.*, 1900, **193**, 1). W. G.

Influence of Bile on Autolysis. ARTHUR L. TATUM (*J. Biol. Chem.*, 1916, **27**, 243—248).—When small blocks of animal tissues are placed in bile and allowed to remain in an incubator for two to four hours, marked autolysis of the peripheral portions occurs, resulting in the disappearance of the cytoplasm. This rapid cytolysis is due to the activating action of the constituents of bile on the autolytic enzymes present in the tissue cells. It does not occur when the block of tissue is boiled before being placed in the bile. Boiled bile is as efficient as fresh bile, and the isolated bile salts exert a similar action, although not so powerful as that exerted by the whole bile. The maximum effects of bile or bile salts are many times greater than the effects of the optimum concentration of acids on autolysis (compare Bradley, A., 1915, i, 1028).

H. W. B.

Vital Dehydrogenation of Succinic Acid in Absence of Oxygen. T. THUNBERG (*Chem. Zentr.*, 1916, ii, 53; from *Zentr. Physiol.*, 1916, **31**, 91—93).—According to Battelli and Stern (A., 1911, ii, 132), succinic acid is reduced by animal organs, the product being, according to Einbeck (A., 1914, i, 773), fumaric acid. The action appears to be one of dehydrogenation proceeding without actual oxidation in presence of a suitable acceptor for the hydrogen (compare Wieland, A., 1913, i, 1304). Wasted muscle was shaken with methylene-blue solution and potassium succinate at 40° after removal of the oxygen in a vacuum; the solution becomes decolorised, whereas in a check experiment with no succinate no change occurs. Instead of Battelli and Stern's name, "succinoxydon," for the enzyme active in this process, the author proposes, therefore, the name *succinodehydrase*. It is noteworthy that potassium cyanide, which in extreme dilutions completely prevents the vital oxidation of succinic acid, does not hinder the decolorisation of methylene-blue in the above experiment.

T. H. P.

Physiological Relation of the Carotin Pigments of Plants to those of the Cow, Horse, Sheep, Goat, Pig, and Hen. LEROY S. PALMER (*J. Biol. Chem.*, 1916, **27**, 27—32. Compare this vol., i, 186).—The blood of animals with pigmented body-fat always contains carotin. In the cases of the cow and horse the carotin is

in combination with albumin in the blood, whereas in the hen it is in a free state. The goat, sheep, and pig, the body-fats of which are colourless, carry only traces of carotin in the blood, even when the diet contains relatively large amounts of carotin. Apparently the carotin in these animals fails to be absorbed from the intestine.

H. W. B.

The Proteins of the Colostrum and Milk of the Cow, and their Relations to Serum Proteins. CHARLES CROWTHER and HAROLD RAISTRICK (*Biochem. J.*, 1916, **10**, 434—452).—The methods for isolation of the proteins are described. They were analysed by the method of van Slyke. It was found that caseinogen, total lactoglobulin, and lactalbumin are sharply differentiated and distinct proteins, and have the same composition whether prepared from colostrum or milk. Milk contains a globulin in small quantities (0·03%). Eulactoglobulin and ψ-lactoglobulin are identical as regards the protein part of their molecule. The lactoglobulin appears to be identical with the serum-globulin of ox-blood, whilst lactalbumin is not identical in composition with the corresponding serum-albumin.

S. B. S.

Volume of Urine in Young Healthy Adults on a Constant Diet. T. ADDIS and C. K. WATANABE (*J. Biol. Chem.*, 1916, **27**, 267—272).—The volume of urine passed by normal individuals on a constant diet with the same water intake is extremely variable for any single day or part of a day.

H. W. B.

Alterations in the Output of Certain Urinary Constituents as Determined by Changes in the Character of the Diet. FRANK P. UNDERHILL and L. JEAN BOGERT (*J. Biol. Chem.*, 1916, **27**, 161—168).—On a diet of maize and oats, the output of phosphorus in the urine of rabbits is far in excess of the intake of this element in the food. Since the hydrion concentration of the urine is very high in these circumstances, the great excess of phosphoric acid in the urine is regarded as an indication of the method of regulating the acid–base equilibrium in the body of the rabbit.

The elimination of ammonia and of calcium under changing conditions of diet is very variable.

H. W. B.

Rate of Excretion of Urea. II. Rate of Excretion of Administered Urea in Young Healthy Adults on a Constant Diet. T. ADDIS and C. K. WATANABE (*J. Biol. Chem.*, 1916, **27**, 249—266. Compare this vol., i, 352).—The rate of excretion of administered urea bears a constant relationship to the actual amount of administered urea within the body. The normal kidney under constant conditions possesses, therefore, a high degree of constancy of function. The repetition of large doses of urea does not elicit the condition known as 'kidney fatigue.' A fraction of the administered urea remains in the body after twenty-four hours. This retention of urea is not due to failure of kidney function, because the amount retained after a 40-gram dose is not greater than that retained after a 20-gram dose of urea.

H. W. B.

The Influence of Flesh Feeding on Urinary Creatinine. DAVID BURNS and JOHN BOYD ORR (*Biochem. J.*, 1916, **10**, 495—503).—The ingestion of flesh causes an increased excretion of creatinine and generally the appearance of creatine in the urine. The amount of increase is not, however, proportional to the amount of flesh taken. Although cooking increases the amount of creatinine in flesh, the ingestion of cooked meat does not cause a larger increase of urinary creatinine than does the uncooked. Pure creatine administered per os is only to a slight extent eliminated as such, and does not markedly alter the creatinine excretion.

S. B. S.

Creatine Metabolism. I. Possible Inter-relations between Acidosis and Creatine Formation. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1916, **27**, 127—139).—The author suggests that the appearance of creatine in urine which accompanies abnormal carbohydrate metabolism may be due to the acidosis which is a concomitant feature of the condition. The withdrawal of carbohydrate from the diet leads to acidosis and also to the elimination of urinary creatine. Certain foods, such as oats and maize, when given to rabbits produce a marked condition of acidosis as measured by the hydrion concentration of the urine. The author finds that in these circumstances, on a diet containing an adequate supply of carbohydrates, creatine promptly appears in the urine of the rabbit. If now a base-producing food, such as carrots, is substituted for the oats and maize, creatine disappears from the urine as it becomes alkaline. The addition of hydrochloric acid to a diet on which the urine of the rabbit remains free from creatine also leads to the appearance of significant quantities of creatine. The author draws the conclusion that a connexion exists between acidosis and creatine elimination. H. W. B.

Creatine Metabolism. II. Influence of Alkali on Creatine Elimination During Inanition. FRANK P. UNDERHILL (*J. Biol Chem.*, 1916, **27**, 141—146. Compare preceding abstract).—The subcutaneous injection of a solution of sodium hydroxide into fasting rabbits greatly diminishes or completely abolishes the associated creatinuria. The effect of the introduction of the alkali is not so marked in the later stages of inanition. H. W. B.

Creatine Metabolism. III. Influence of Alkali on the Creatinuria of Phloridzin Glycosuria. FRANK P. UNDERHILL and EMIL J. BAUMANN (*J. Biol. Chem.*, 1916, **27**, 147—150. Compare preceding abstract).—The administration of sodium hydrogen carbonate in gelatin capsules to phloridzinised dogs does not reduce the elimination of creatine. The author draws the conclusion that in this condition the tendency for acid production is too great to be controlled by administration of alkali. H. W. B.

Creatine Metabolism. IV. Relationship of Creatinuria to Carbohydrate Metabolism and Acidosis. FRANK P. UNDERHILL and EMIL J. BAUMANN (*J. Biol. Chem.*, 1916, **27**, 151—160. Compare preceding abstracts).—The creatinuria induced by the sub-

cutaneous administration of hydrazine to dogs is associated with hypoglycæmia and marked alkalinity of the urine. The author draws the conclusion that although creatine may appear in the urine during states of acidosis (*loc. cit.*), creatinuria may also be present in the absence of acidosis when the utilisation of carbohydrates in the body is interfered with in the manner occurring after the administration of hydrazine (compare Underhill and Hogan, A., 1915, i, 475). H. W. B.

Creatinuria in Children. FRANK POWIS and HENRY STANLEY RAPER (*Biochem. J.*, 1916, **10**, 363—375).—It was found, in a normal boy two and a-half to three years of age, that the rate of excretion of creatinine is slightly less during the night than during the day. The rate of excretion of creatine is highest during the morning, less during the later part of the day, and very small at night. If 0·1 gram of creatine is given at the beginning of the morning, most of it is excreted in the following twelve hours, but if the same amount is given at bed-time, there is no increase in creatine excretion. The higher excretion of creatine during the day is not due to acidosis, as the percentage of total nitrogen present in the urine as ammonia is less during the day than during the night. S. B. S.

The Distribution of Nitrogen in the Proteins of Tumours and of Normal Tissues. JACK CECIL DRUMMOND (*Biochem. J.*, 1916, **10**, 473—494).—Details are given of a large number of analyses of tumours and normal tissues by the van Slyke method. The tumours included a considerable number of human origin and also Rous tumours of chicken. The results indicate that the diamino-acid content of a tissue varies with the amount of nuclear material present; the more rapidly growing and cellular tumours show, therefore, a higher content of these substances than do the slowly growing ones.

There is no evidence from the analysis of the proteins of malignant tumours that the hexone bases are responsible for an increased rate of cell division. S. B. S.

The Cause of Lessened Production of Indole in Media containing Dextrose. ANNIE HOMER (*J. Hygiene*, 1916, **15**, 401—404).—It is suggested that the sugar, as aldehyde, forms a compound with tryptophan, which is less readily attacked than tryptophan itself. G. B.

The Action of Hypochlorites and Allied Substances on Proteins and their Behaviour on Injection. THOMAS HUGH MILROY (*Biochem. J.*, 1916, **10**, 453—465).—The loss of available chlorine when solutions of magnesium hypochlorite and chloramine-T (sodio-*p*-toluenesulpho-chloroamide) are treated with serum proteins, amino-acids, etc., was investigated. It was found that there was a marked difference between the behaviour of the hypochlorites and the chloramine. The former acted very readily

on proteins until only 10% of the available chlorine was left in the solution, after which the action was slow. The loss of available chlorine from chloramine solutions was much slower, and the rate is much more dependent on the amount of serum added, varying directly with this amount. It is suggested that for these reasons the hypochlorites, owing to their more rapid initial action, may be of greater value for primary disinfection of wounds and result in a more efficient penetration and oxidation of necrosed material, whereas where longer intervals elapse between dressings of the wounds solutions of chloramine would be an advantage.

The effects of hypochlorites and chloramine on the blood corpuscles and blood pressure in animals were also investigated. They cause laking and lowering of blood-pressure, the effect of chloramine on the latter factor being greater than that of hypochlorites. It is inadvisable to inject chloramine in concentrations greater than 0·2%. No hæmolysis results from such an injection when the chloramine concentration is not raised above 1/1200. S. B. S.

The Four Carbon Atom Acids of Diabetic Urine. WILLIAM HOLDSWORTH HURTLEY (*Quart. J. Med.*, 1916, **9**, 301—408).—Mainly clinical and dietetic, with an extensive review of the literature and bibliography. Hexose–phosphoric acid of Harden and Young was administered in some cases; it probably has a slight effect in diminishing the output of sugar in the urine. It is suggested that the toxicity of acetoacetic acid and that of salicylic acid is due to the grouping $HO\cdot C{=}CH$:

$$\begin{array}{l} CH{:}CH\cdot C\cdot OH \\ \;| \qquad\quad \| \\ CH{:}CH\cdot C\cdot CO_2H \end{array} \quad \text{and} \quad \begin{array}{l} CH_3\cdot C\cdot OH \\ \qquad\;\; \| \\ \quad H\cdot C\cdot CO_2H \end{array}.$$

G. B.

Physiological Action of Acetoacetic Acid and Related Substances. W. H. HURTLEY and J. W. TREVAN (*Proc. Physiol. Soc.*, July 15th, 1916; *J. Physiol.*, **50**).—In connexion with the hypothesis of the preceding abstract, the physiological actions of ethyl and sodium acetoacetate, of acetylacetone, and of sodium salicylate have been investigated. In intact animals acetylacetone produces symptoms of diabetic coma. In decerebrate animals hyperpnœa is produced with the mid-brain intact, apnœa if the latter is destroyed. G. B.

General Reaction of Amino-acids in the Animal Organism: Decomposition of Proteins and Formation of Carbamide. DOMENICO LO MONACO (*Chem. Zentr.*, 1916, ii, 22; from *Arch. Farm. sperim.*, 1916, **21**, 121—128).—According to Schmiedeberg's theory, carbamide is formed in the organism from ammonium carbonate, of which the components, ammonia and carbon dioxide, must arise from scission of proteins. The latter give such components outside of the organism, under the influence of artificial and natural catalysts, but their formation in the normal animal organism has not previously been observed.

The author now shows that the amount of ammonia in the urine is increased by subcutaneous injection or, even more markedly, by ingestion of amino-acids. It has not been found possible to measure exactly the extent of this increase, since the latter is augmented by rest and lowered by movement of the body. Alanine, glycine, phenylalanine, and phenol alone and also in conjunction with alanine or leucine, were examined subcutaneously and phenylalanine, zein, and dry egg-albumin by ingestion. The ammonia-content of the urine is increased most by phenylalanine; the assumption that this is caused by a special action of the phenyl residue on the stability of the molecule is indicated by the results of the experiments with phenol. Consequently, substances rich in this group do not appear well fitted for nutriment. The proteins yielding much phenylalanine on hydrolysis include zein, which increases considerably the excretion of ammonia in the urine. The corresponding low value of zein may serve to explain the phenomena accompanying nutrition with maize alone. T. H. P.

Toxicity of Carotin. H. Gideon Wells and O. F. Hedenburg (*J. Biol. Chem.*, 1916, **27**, 213—216).—The authors have investigated the physiological action of carotin and chlorinated carotin, the pigments occurring in ordinary flour and bleached flour respectively. Intraperitoneal injection of large quantities of either pigment into guinea pigs does not produce any toxic effect, even when the dose is as much as the amount normally contained in 200 kilos. of flour. Similar results after subcutaneous injections indicate that carotin, whether in its natural state or saturated with chlorine, is entirely devoid of toxicity. H. W. B.

Some Experiments on Glyoxaline Derivatives. George Barger and Henry Drysdale Dakin (*Biochem. J.*, 1916, **10**, 376—381).—(1) Glyoxalinealdehyde was administered to a dog. Glyoxalinecarboxylic acid could be isolated from the urine subsequently excreted. This conversion of the glyoxalinealdehyde into the abovementioned acid is analogous to the formation of pyromucic acid in the body from furfuraldehyde as observed by Jaffé and Cohn.

(2) When glyoxalinealdehyde is warmed with malonic acid in aqueous solution, a condensation product is readily formed without the addition of a catalyst according to the equation:

$$CH\begin{matrix}\diagup NH\cdot CH \\ \diagdown N\text{---}\overset{||}{C}\cdot CHO\end{matrix} + CH_2(CO_2H)_2 =$$

$$CH\begin{matrix}\diagup NH\cdot CH \\ \diagdown N\text{---}\overset{||}{C}\cdot CH{:}C(CO_2H)_2\end{matrix} + H_2O$$

Glyoxalinemethylenemalonic acid thus obtained has m. p. 214°. All attempts to prepare urocanic acid from this by heating have failed.

(3) An attempt was made to prepare glyoxalineacetaldehyde by heating α-hydroxy-β-glyoxalinepropionic acid with sulphuric acid. The chief reaction takes place, however, according to the equation: $2C_6H_8O_3N_2 = C_{10}H_8N_4 + 2CO + 4H_2O$. The base formed crystallises

with $1H_2O$ from hot water, in which it is only sparingly soluble. The anhydrous *base* has m. p. 235—238°. Its *nitrate* is only slightly soluble in water. S. B. S.

Intravenous Injection of Sodium Gynocardate in Leprosy. LEONARD ROGERS (*Brit. Med. J.*, 1916, ii, 550—552. Compare T., 1904, **85**, 838, 851).—The fraction of lower melting point (up to 40°) of the fatty acids of chaulmoogra oil from the seeds of *Taraktogenos kurzii* is the most useful in treatment of leprosy. This so-called gynocardic acid is best given intravenously as sodium salt. The fraction of m. p. 40·8—43° with sodium salts scarcely soluble in water, contains chaulmoogric acid, which is unsuitable for injection and probably therapeutically useless. G. B.

Inter-relations of Blood-fat and Blood-sugar Content of Dogs under the Influence of Hydrazine. FRANK P. UNDERHILL and EMIL J. BAUMANN (*J. Biol. Chem.*, 1916, **27**, 169—172).—After the administration of hydrazine to dogs, the fat in the blood is markedly increased, the maximum being coincident with the condition of hypoglycæmia characteristic of hydrazine poisoning. H. W. B.

Phenylethylhydantoin (Nirvanol), a New Hypnotic and Sedative. E. WERNECKE (*Deut. med. Woch.*, 1916, **42**, 1193—1194). —$\gamma\gamma$-Phenylethylhydantoin dissolves in 1650 parts of cold, and in 110 parts of hot, water, in 20 parts of spirit; it has a hypnotic action of about the same intensity as phenylethylbarbituric acid (luminal), but is distinctly less toxic. Its hypnotic action is greater than that of diethylbarbituric acid (veronal). G. B.

Chemistry of Vegetable Physiology and Agriculture.

Vital Stains with the Simplest Dyes, and their Fixatior SIEGFRIED SKRAUP (*Ber.*, 1916, **49**, 2142—2154).—The author has applied a large number of dyes, principally of simpler types, to the staining of protoplasm in living organisms, such as amœba, paramœcium, and actinosphærium, and finds that there is no specific chemical factor which controls the union of the protoplasm with the dye. The governing consideration is the colloidal nature of the dye, for within the limits of any particular group of dyes the more diffuse dye is the less powerful as a stain. The modern views that dyeing is merely an adsorption phenomenon are therefore held by the author. The dispersoid nature of a dye is vitally influenced by its chemical constitution and can also be modified by the addition of an appropriate salt. Neat differentiations of the

staining by a somewhat diffuse dye can therefore be achieved by the addition of different salts.

It is also found that any vital stain can be fixed if the dye forms a tolerably insoluble compound with the fixing agent. Thus basic dyes can be fixed by mercuric chloride and phenolic dyes by lead acetate, facts which are of practical interest to pathologists and biologists. J. C. W.

Action of Sulphur and Calcium Sulphate on Certain Higher and Lower Forms of Plants. WALTER PITZ (*Bied. Zentr.*, 1916, **45**, 393—394; from *J. Agric. Research*, 1916, **5**, 771).—Calcium sulphate added to soil had no appreciable action on bacteria in agar-agar cultures, and there was no appreciable increase in the production of ammonia and nitrates. Large amounts of sulphur decreased the number of bacteria on agar plates, and up to 0·05% increased ammonia production, whilst the production of nitrates was retarded.

Calcium sulphate (0·01—0·1%) promotes the growth of red clover bacteria in nutritive solutions; the same amounts also increase the growth of the roots of red clover. The yield of red clover and the number of root-nodules is increased by small amounts of calcium sulphate.

On a sandy loam soil, applications of 0·01% of sulphur slightly increased the yield of red clover, without, however, influencing the development of roots and root-nodules. Similar results were obtained with larger amounts of sulphur. N. H. J. M.

Nutrition of Yeast with Glycerol; also with other Alcohols. TH. BOKORNY (*Chem. Zentr.*, 1916, i, 1174—1175; from *Allg. Brau. Hopf.-Zeit.*, **56**, 177—180, 195—196).—Glycerol is able to supply yeast with its carbonaceous nutriment, and acts best in presence of sugar, since otherwise putrefactive organisms grow readily in the medium. This result is in contradiction to the conclusion drawn by Ehrlich. Experiments have been made on the nutrition of yeast with the combinations tyrosine–glycerol–sugar and tyrosine–sugar, peptone–glycerol–sugar and peptone–sugar, and also others in which asparagine, leucine, aspartic acid, glycine, glutamic acid, and carbamide were used, in all cases in presence of sugar. The results obtained show that tyrosine is a source of nitrogen for beer-yeast, and that glycerol in the combination glycerol–asparagine furnishes the yeast with carbon, although with glycerol–tyrosine this is doubtful. With the other nitrogen compounds mentioned above, the yeast shows a greater increase in the amount of dry matter in presence of glycerol than in its absence. Ethylene glycol, methyl, ethyl, propyl, amyl, and benzyl alcohols, phenol, and catechol do not serve as sources of carbon in the nutrition of yeast. Quinol in 0·05% concentration allows of the growth of moulds, but not of yeast, and the latter cannot be cultivated in gallic acid or pyrogallol solution; 0·01% of cresol or xylenol is poisonous to yeast. T. H. P.

Sensitiveness of Certain Beer-yeast Enzymes. TH. BOKORNY (*Chem. Zentr.*, 1916, i, 1261—1263; from *Allg. Brau. Hopf.-Zeit.*, **56**, 395—397, 433—434, 465—468).—The author has investigated the effect of a large number of reagents on the action of the following enzymes occurring in yeast: invertase, maltase, zymase, rennin, and myrosin.

Even when allowed to act on yeast for several days, absolute alcohol does not injure the invertase, provided that it is removed prior to the examination of the inverting capacity of the yeast. The opposite result obtained by Hudson and Paine (A., 1910, i, 798) is explained by the high temperature (30°) used by these authors in their experiments and by the non-removal of the alcohol. Zymase and yeast are destroyed by 50% alcohol. Yeast–rennin is one of the heat-resistant enzymes. For the many other results obtained reference must be made to the original. T. H. P.

The Evolution of Oxygen Arising from the Reduction of Nitrates by Green Plants. MARIN MOLLIARD (*Compt. rend.*, 1916, **163**, 371—373).—Comparative tests on growing radishes in sealed flasks fitted with a manometer and containing culture solutions differing only in the form of nitrogen supplied, ammonium chloride in one case and potassium nitrate in the other, indicate that, with the potassium nitrate, for every atom of nitrogen fixed two atoms of oxygen are liberated. W. G.

Mechanism of Absorption of Salts in Plants. E. PANTANELLI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1915, [iii], **21**, 55—63).—The author has made extensive series of experiments on the absorption of many different salts from their solutions by fresh-water plants, terrestrial plants, yeast, and marine algæ. The last two classes of organisms were totally immersed in the solutions, whilst only the roots of the land plants were immersed after the plants had been reared in nutrient solutions. The principal results obtained are briefly as follows.

In various cases, the two ions of a salt are absorbed proportionally, the absorption being apparently one of undissociated molecules. In all such cases, however, either the salt contains a toxic ion which alters or tends to alter the osmotic properties of the plasma, as is shown by the subsequent behaviour of the same cells towards plasmolytic agents, towards the penetration of dyes, etc., or both ions have nutrient properties, or both have toxic or unfavourable properties. That the proportional absorption of the ions in even these rare instances is accidental is shown by the fact that the same ions in the same salts are absorbed by some plants in equivalent proportions, whereas by other plants, or even by the same plants under different external or internal conditions, they are absorbed in proportions quite different from those corresponding with undissociated molecules. In some cases the cation and in others the anion is absorbed the more, in accordance with the preference which each species of plant exhibits.

Comparison is drawn between the results obtained with two salts

having one common ion, whilst the other ion is harmful in one case and, although similar, nutrient or useful in the other, for instance, with barium and calcium chlorides, lithium and potassium nitrates, ammonium and potassium sulphates, zinc and magnesium sulphates, potassium arsenate and phosphate. In most cases there is complete independence in the absorption of the two ions, the useful cation penetrating with the same rapidity in presence of a nutrient anion as if accompanied by a poisonous anion; the latter, however, remains outside, whereas the nutrient anion enters the plant in large amount. Similar relations govern the behaviour of a useful anion towards nutrient and harmful cations. In a few instances, the absorption of a nutrient cation was found to be restricted by the presence of a harmful anion, and vice versa, but the various organisms examined do not show uniform behaviour in this respect. No case has been observed in which the absorption of a toxic ion is facilitated by an accompanying nutrient ion.

The influence of narcotics on this absorption has also been studied. As a rule, cells slightly narcotised (with 0·05% chloral hydrate solution) absorb less cation, but cases are not rare, with poisonous cations, where the narcotised cells show increased absorption. Similar observations have been made for anions, and it would appear that the explanation of the phenomena of antagonism between salts and anæsthetics advanced by various authors is not supported experimentally, but further examination of this point is necessary. The principal result of the author's tests in this direction is that chloral (or chloroform or ether) exerts unequal influences on the absorptions of the two ions of one and the same salt, as regards not merely the magnitude, but also the sense of the variation. Since nutrient ions are absorbed less and adverse ions more in presence of a narcotic, proportional absorption of the two ions, that is, apparent absorption of the whole molecule, may occur more easily with narcotised cells than with cells in full possession of the selective faculty.

During the initial stages of the growth of plants in these salt solutions, increase of acidity or alkalinity of the external solution occurs in consequence of the predominating absorption of one of the two ions. After some hours, or maybe days, the cell exhibits the power to develop in the liquid a more favourable degree of acidity, this being attained by the excretion of other ions; this effect is most marked with the marine algæ.

Whilst those ions which readily enter the cells do so with such rapidity that the concentration inside may exceed that outside after a few moments, those showing the opposite behaviour do not, as a rule, reach a state of equilibrium except in those cases where they are supplied in toxic concentration and alter completely the osmotic properties of the plasma. Further, the absorption of ions of the first type is not continuous, but resembles the damped vibration of a pendulum, a large and vigorous absorption being followed by a partial excretion of the same ion and then by a second smaller absorption and an excretion, and so on, these processes being repeated until a definite proportion is established

between the internal and external concentrations of the particular ions.

The curves connecting the proportion of ion absorbed under similar conditions with the concentration are typical adsorption isotherms for all ions, although the curves for the two ions of a salt do not coincide and vary with the specific organism and with other factors. The relative diminution of the absorption begins to become apparent when the concentration approaches the toxic strength for poisonous ions and the plasmolytic limit for non-toxic ions. If the concentration is increased still further, the relative absorption increases rapidly, giving a second curve which also follows the laws of adsorption, but the penetration of the ions under these conditions is evidently not a physiological phenomenon, but is due to alteration of the protoplasm (compare Lavison, A., 1910, ii, 1100).

As regards the mechanism of these processes, the conclusion is drawn that the absorption of salts insoluble in the lipoids is possible only in so far as these salts are dissociated. The absorption is facilitated by the presence of H' or $OH^{\bullet}$ ions in the external solution or in the plasma, the adsorption potential at the limiting surface being thereby increased. Confirmation is obtained of the independence of the absorption of water from that of the ions present in it, cellular colloids thus exhibiting the property of negative adsorption. T. H. P.

Permeability of Living Cells to Acids and Alkalis. A. R. Haas (*J. Biol. Chem.*, 1916, **27**, 225—232. Compare Crozier, this vol., i, 694).—The author has investigated the penetration of acids and alkalis by means of natural indicators contained in the petals of *Browallia speciosa* and of *Pelargonium*, the perianth of "Queen of the Blue" hyacinth, and the root of the red radish. It is found that the relative rate of penetration of the hydrogen ion in $N/100$-solutions (made by titration) of acids and alkalis is practically the same in the plants studied as that found in the case of animal tissues (*loc. cit.*). When, however, the solutions are prepared with a hydrogen ion concentration of $N/100$ (by the use of the gas chain), very different results are obtained, depending partly on the dissociation of the acids concerned. The concentration of the hydrogen or hydroxyl ion is not, therefore, the only factor governing penetration. H. W. B.

Acidity of Plant Cells as shown by Natural Indicators. A. R. Haas (*J. Biol. Chem.*, 1916, **27**, 233—241).—The hydrion concentration in pigmented plant cells is estimated by adding aqueous or alcoholic extracts of the plant tissues to buffer solutions of known hydrion concentration and ascertaining in which solution the natural colour remains unchanged. The results clearly indicate that the reaction of the cell sap is usually acid. Even cells containing blue pigments are usually acid, although in some cases a neutral to very slightly alkaline reaction was obtained. As the

cell dies, a considerable change in the hydrion concentration may occur, which is revealed by a change in the colour of the petal or other plant tissue. H. W. B.

The Constituents of Wood which give Colour Reactions. H. WICHELHAUS and M. LANGE (*Ber.*, 1916, **49**, 2001).—If wood is submitted to a current of steam at 180°, hydrolytic products, which give the well-known colour reactions with phloroglucinol and hydrochloric acid, are found in the distillate. It is proposed to investigate these (compare Grafe, A., 1905, i, 22). J. C. W.

Applied Plant Microchemistry. XII. Microchemistry of Gentisin and of the Yellow Colouring Matter in Frasera carolinensis. O. TUNMANN (*Chem. Zentr.*, 1916, ii, 65—66; from *Apoth. Zeit.*, 1916, **31**, 181—182, 189—190).—For the identification of gentisin, the microcrystalline forms of the latter and of its alkali salts, and of the compounds obtained with (1) sulphuric and nitric acids, and (2) bromoacetic acid, are employed; a sublimate is better for this purpose than separate crystals of gentisin.

These reactions have been used to examine the distribution of gentisin in the different organs of the gentians and of *Frasera carolinensis.* The flowers of *Gentiana pupurea-punctata* contain, in relatively large proportion, a new *compound*, which sublimes at about 180° in colourless, flat, prismatic bars and plates, and is probably a higher, aliphatic alcohol.

The yellow colouring matters of *Frasera carolinensis* may be sublimed undecomposed directly from the different parts of the plant. In the root, these colouring matters occur in the parenchyma and in the calyx and corolla, in the epidermis and mesophyll; in the seeds, they occur regularly and in large quantity in every cell of the plumule. From the crystalline forms of various derivatives which have been obtained, the conclusion is drawn that three different colouring matters occur, one of them only in traces. T. H. P.

[The Oil of] Hydnocarpus Venenata, Gaertner. False Chaulmoogra [Oil]. HARVEY C. BRILL (*Philippine J. Sci.*, 1916, **11**, [*A*], 75—80).—The oil of *Hydnocarpus venenata* has the following constants: m. p. 20°, $D^{30°}$ 0·948, n_D 1·477, $[\alpha]_D$ 52·03°. Iodine number 99·1, acid number 4·4, saponification number 200·3. Chaulmoogric acid, $C_{17}H_{31}CO_2H$, and hydnocarpic acid,

$$C_{15}H_{27}\cdot CO_2H,$$

are present, in addition to a cyanogenetic glucoside. Its chemical composition and constants are therefore similar to those of the oils of *H. wightiana*, *H. anthelminticus*, and *Taraktogenos kurzii*, the latter of which is the true chaulmoogra oil, and their physiological properties should accordingly be identical. The properties of the oil of *Gynocardia odorata* may be different according to whether the physiological activity is due to the unsaturated acids present in the hydnocarpus oils or to the glucoside present in all the oils. G. F. M.

Nitrogen Compounds of Mulberry Leaves. YETSUO KATAYAMA (*Bull. Imp. Sericult. Exper. Stat., Nakano, Tokyo*, 1916, **1**, 1—30).—From 1 kilo. of the dried leaves, the following amounts of the various nitrogen compounds were obtained: glycine, 0·06; alanine, 1·0; valine, 0·47; leucine, 0·60; proline, 0·05; aspartic acid, 5·20; phenylalanine, 0·60; guanine, 0·10; adenine, 0·52; hypoxanthine, 0·12; histidine, 0·20; arginine, 1·30; lysine, 0·93; choline, 1·90; and trigonelline, 0·2 gram. Tyrosine was also found.

When hydrolysed, about 90% of the total nitrogen dissolved, of which 50% belonged to monoamino-acids and 35% to bases.

After hydrolysis, 1 kilo. of dried leaves yielded: leucine, 21·0; alanine, 19·0; valine, 10·5; arginine, 8·8; lysine, 6·6; aspartic acid, 6·0; proline, 2·5; phenylalanine, 2·5; choline 2·3; serine, 2·0; glycine, 1·5; and histidine, 1·3 gram.

The composition of the nitrogenous portion of mulberry leaves differs considerably from that of the cocoons (Inouye and Iwaoka, *J. Tokyo Chem. Soc.*, 1915, **36**). N. H. J. M.

Carbohydrates of the Musci. THOMAS G. MASON (*Sci. Proc. Roy. Dublin Soc.*, 1916, N.S., **15**, 13—28).—The following Musci were investigated: *Polytrichum commune, Thuidium tamariscinum*, and *Sphagnum cymbifolium.* Dextrose, lævulose, and sucrose were found in all the materials examined, whereas maltose is dependent on the presence of starch. Diastase and maltase were found only in *Polytrichum commune;* invertase is widely distributed. In *P. commune* and *Sphagnum cymbifolium* the carbohydrates seem to descend the stem chiefly in the form of hexoses. N. H. J. M.

Rennin from Solanum Elaeagnifolium. A. BODANSKY (*J. Biol. Chem.*, 1916, **27**, 103—105).—The rennin from the berries of *Solanum Elaeagnifolium* closely resembles ordinary rennin from animal sources. H. W. B.

Poisonous Action of Lithium Salts on Plants. H. FRERKING (*Chem. Zentr.*, 1916, i, 1252; from *Flora*, 1915, **8**, 449—453).—Lithium acts as a poison only towards plants which need calcium and not towards the calcium-free lowest algæ and fungi. The poisonous action of lithium is stronger than that of magnesium. In the latter case, the poisonous effect is removable by addition of calcium salts, whereas these only retard the poisonous action of lithium salts. T. H. P.

Translocation of Seed Protein Reserves in the Growing Maize Seedling. C. J. V. PETTIBONE and CORNELIA KENNEDY (*J. Biol. Chem.*, 1916, **26**, 519—525).—During the growth of the maize seedling the total nitrogen of the seed diminishes, whilst that of the plumule and root increases, the total nitrogen in the seedling remaining fairly constant. The amino-acid nitrogen in seed, plumule, and root remains at a more or less constant value. A careful examination of the sap shows the presence of free amino-acids, as well as of traces of soluble proteins or peptides. These results indicate clearly that the transportation of the reserve proteins of the seed to furnish material for the proteins of the growing

parts of the plant takes place in the form of amino-acids in a manner analogous to the similar process occurring in the animal organism. H. W. B.

Relation of Amide Nitrogen to the Nitrogen Metabolism of the Pea Plant. BARNETT SURE and W. E. TOTTINGHAM (*J. Biol. Chem.*, 1916, **26**, 535—548).—In the early stages of growth, amides and amino-acids accumulate in the cotyledon and in the growing shoot. Later on, the amino-acids decrease considerably in the shoot and completely in the cotyledon, whilst at the same time the amides rapidly increase in both parts of the plant. The authors draw the conclusion that the amino-acids serve for amide production in the nitrogen metabolism of the etiolated pea plant. H. W. B.

The Salicylic Acid Reaction of [Soja] Beans. HARVEY C. BRILL (*Philippine J. Sci.*, 1916, **11**, A, 81—89).—Soja beans give the ferric chloride colour test for salicylic acid, but this is not conclusive evidence that this substance is present either initially or as an added preservative. Moreover, although alcoholic extracts of numerous samples of Chinese, American, and Japanese beans, and preparations therefrom, on extraction with ether, gave the ferric chloride test, they failed to give the Jorissen salicylic acid test, which was shown to be equally delicate. The conclusion is therefore drawn that the substance giving the violet colour is not salicylic acid, but a product similar to maltol, and it is probably formed by enzyme action in the beans. G. F. M.

Wine containing Free Sulphuric Acid. W. I. BARAGIOLA and O. SCHUPPLI (*Zeitsch. anal. Chem.*, 1916, **55**, 369—377. Compare this vol., ii, 488).—About 0·1% of free sulphuric acid was present in an Alsatian white wine (1889 vintage) examined by the authors. W. P. S.

Causes of Acidity of Soils which are Acid through Exchange of Ions. H. KAPPEN (*Landw. Versuchs-Stat.*, 1916, **89**, 39—80; Compare *ibid.*, **88**, 13).—Two pine-forest soils and a soil on which the vegetation consisted of a few bilberry shrubs were investigated. The forest soils, which were covered with a layer of humus, 2—3 cm. deep, showed considerable activity when treated with a iormal solution of potassium chloride; the third soil failed to react with potassium chloride. The latent acidity of the forest soils is attributed to the action of humic acids on the mineral soil and the production of aluminium and iron salts.

It is shown that the true acidity of humus extracts is approximately the same as that of acetic acid of the same strength, and that latent acidity can be produced by treating mineral soils with raw humus. The same result is obtained with some vegetable substances which are only partly humified.

Latent acidity can perhaps also arise from the production of soluble iron and aluminium compounds in the humus itself and the penetration of the soluble salts into the mineral soil below the humus. N. H. J. M.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

The Relationships between the Index of Refraction and the Density of some Gases. C. STĂTESCU (*Bull. Sci. Acad. Roumaine*, 1915, **4**, 175—184).—Working with dried air, oxygen, and carbon dioxide, the author has determined the values of the fraction $(n^2-1)\delta$ in Newton's law and $(n^2-1)/(n^2+2)\delta$ in Lorentz's law for varying conditions of pressure and wave-length. Working with dried air and varying only the pressure, the author shows that these fractions are constant, and that in consequence the natural frequency of the particles (electrons or ions) of the individual molecule must be affected by the pressure in the same measure as the structure. Keeping the temperature and pressure constant, but varying the wave-length of the light, he finds that for air and oxygen, which show no absorption bands in the infra-red, the values of the fractions diminish with increase in wave-length. For carbon dioxide, which has absorption bands at $\lambda=4{\cdot}27\ \mu$ and $14{\cdot}7\ \mu$, it is shown that the values of the fractions exhibit the same discontinuity in these directions as does the variation in dispersion.

W. G.

Two Burners for the Demonstration and Study of Flame Spectra. PHILIP E. BROWNING (*Amer. J. Sci.*, 1915, [iv], **40**, 507—508).—Into a wide-mouthed bottle fitted with a three-hole stopper is placed a piece of the, preferably natural, carbonate of the metal (barium, strontium, or calcium) and sufficient water to cover it. A thistle funnel dips below the surface of the liquid,

and through the other holes in the stopper pass a tube connected with the gas supply, and a second tube drawn out into a jet over which a porcelain tube is suspended and adjusted so as to produce a colourless flame at its exit. Acid is then added through the thistle funnel to start a gentle evolution of carbon dioxide, which carries sufficient of the solution in suspension to be swept by the gas into the flame and to impart to it a colour of some permanence. A modified form of apparatus is preferable for sodium, potassium, and lithium. The thistle funnel is replaced by a glass tube in which a glass rod, attached by a rubber connector, slides up and down. To the lower end is attached a piece of zinc, which can thus be lowered into acid contained in the bottle. The hydrogen thus generated carries the metallic salt, which is dissolved in the dilute acid, into the flame. G. F. M.

The Nature of the Vibrations Causing the Colour of Dyes. EDWIN ROY WATSON and DAVID B. MEEK (T., 1915, **107**, 1567—1578). —Observations already made (T., 1914, **105**, 759) showing that such dyes as are quinonoid in all possible tautomeric forms exhibit a deep colour if different benzene nuclei become alternately quinonoid, whilst dyes which have a long chain of alternate double and single bonds in the quinonoid form are generally deeply coloured, have led to the suggestion that the nature of the vibrations causing the colour of dyes may be likened to a pulse along a molecule due to the successive breaking and making of the double bonds, in something the same way that a movement would travel along a venetian blind when a finger is passed up or down the louvres. If this be the case, it might be expected that the frequency of the vibration in a particular compound would be proportional to the length of the chain of single and double linkings. Seven pairs of compounds have been examined, each pair similar in structure, but with these conjugate chains of different lengths. Thus, in 4 : 4′-tetramethyldiaminobenzhydrol there are five double bonds, whilst in 4 : 4′-tetramethyldiaminobenzophenone there are three. It might therefore be expected that the frequency of vibration in the two substances would be inversely as five to three, or that the wave-lengths of the heads of the absorption bands should be directly as five to three. This is actually found to be the case, the wave-lengths of the maxima of the absorption bands lying at 6100 and 3680 respectively, a ratio of 1·65, thus agreeing closely with the theory. A similar agreement is found in the case of 4 : 4′-diaminobenzhydrol and 4 : 4′-diaminobenzophenone, and also between quercetin, morin, apigenin and their respective reduction products. In pyronine-*G* and 3 : 6-tetramethyldiaminoxanthone, and also in 3-hydroxyfluorone and 3 : 6-dihydroxyxanthone, the ratio four to three was found. This, although unexpected, agrees with possible formulæ for these compounds. The authors' theory is then discussed in regard to the work of other investigators. T. S. PA.

The Effect of Additional Auxochromes on the Colour of Dyes. I. Phthalein and Benzein Dyes. VISHNU RAM MEDHI and EDWIN ROY WATSON (T., 1915, **107**, 1579—1582).—Following

up some previous work (T., 1914, **105**, 766), fluorescein, gallein, dihydroxyfluorescein, resorcinolbenzein, pyrogallolbenzein, and hydroxyquinolbenzein have been investigated spectroscopically in alcoholic solution with and without the addition of potassium hydroxide. The results are shown in diagrams. It is found that the effect of increasing the number of auxochromes is to widen the absorption band in the visible spectrum, and to shift the maximum towards the red. The results are interpreted as due to two absorption bands, the relative strengths of which are different in the several cases. These two bands may be due to different tautomeric forms of the substances present in different proportions under different conditions, or they may be due to two different modes of vibration of the dye molecules which only exist in one form.

T. S. PA.

Baly's Experimental Observations Relating to the "Force Field Theory." A. HANTZSCH (*Ber.*, 1915, **48**, 1327—1332).—A criticism of the observations which have been advanced in support of the force field theory as a basis for the interpretation of changes in the absorption spectra of solutions produced by the addition of various reagents. In some cases, it is stated, the absorption measurements are incorrect, and in others the observed changes in the absorption are due to impurities in the substances examined. For instance, the change of yellow to red of an alcoholic solution of azobenzenetrimethylammonium iodide on the addition of 1% of hydrogen chloride (Baly and Hampson, T., 1915, **107**, 248) is attributed to the presence of dimethylaminoazobenzene. Again, the disappearance of the absorption of ethyl acetoacetate in aqueous solution when the concentration is reduced to $N/1000$ (Baly and Rice, T., 1913, **103**, 91) is supposed to be due to the presence of alkali in the solvent.

The author contends that there is no evidence whatever for the force field theory, and that all established changes in the absorption spectra are due to chemical changes which result in the formation of new compounds.

H. M. D.

The Relation between the Configuration and Rotation of Epimeric Monocarboxylic Sugar Acids. P. A. LEVENE (*J. Biol. Chem.*, 1915, **23**, 145—146).—The author applies the principle of Hudson regarding the relationship between configuration and rotatory power to the epimeric acids derived from the sugars. These differ from one another only in the configuration of the α-carbon atom, and as regards this atom are antipodes. If the magnitude of the rotation due to this atom is A, and that of the sum of the other asymmetric carbon atoms is B, then the following relationships are deduced: $B=(M+N)/2$, $A=(M-N)/2$, where M and N are the empirical values. In cases where the free acids are unstable (for example, form lactones) the salts of the same base of the epimerides may be employed for the determination of rotations. Examples of the method are given, which may be employed to ascertain the configuration of substances where chemical methods are not available.

S. B. S.

Fluorescence of Solutions. G. LÉPINE (*Ann. Physique*, 1915, [ix], **4**, 207—228).—The fluorescence of solutions of a number of substances in various solvents has been studied by means of a modified Laurent colorimeter at a series of concentrations. In the case of relatively concentrated solutions of rhodamine and phenosafranine in alcohol and fluorescent-blue in water, of concentration $1 \times 10^{-7} - 1 \times 10^{-5}$ grams per c.c., it is shown that at the lower concentrations the fluorescence is a linear function of the concentration, but that at the higher concentrations it approaches a maximum. With solutions of uranine in methyl alcohol, uranine, rhodamine, and fluorescent-blue in water, of concentrations 3×10^{-8} to 2×10^{-9}, the results are less definite on account of experimental difficulty, but in general the linear relationship between fluorescence and concentration is observed. The influence of the solvent on fluorescence has been studied for solutions of phenosafranine, rhodamine, fluorescent-blue, Magdala-red, eosin, and erythrosine in water, methyl, ethyl, *iso*butyl and amyl alcohols, acetic acid, acetaldehyde, acetone, glycerol, ethyl ether, pyridine, benzene, ethylene dibromide, ethyl acetate, chloroform, and nitrobenzene. It is shown that the relationship is very complex; in some cases the ratio of the fluorescence in different solutions of the same concentration is 1 : 15. The alcohols, acetone, acetaldehyde, ethyl acetate, and acetic acid always yield strongly fluorescent solutions. Acetic acid gives no fluorescence with substances which lose their fluorescence when treated with acids. Glycerol solutions present a medium fluorescence, and pyridine, chloroform, and ethylene dibromide give a feeble fluorescence. Nitrobenzene and water behave differently with the various substances. Thus aqueous solutions of rhodamine are strongly fluorescent; aqueous solutions of fluorescent-blue, eosin, and erythrosine have a medium fluorescence, and an aqueous solution of phenosafranine is very feebly fluorescent. A series of experiments on the relationship between fluorescence and absorption of light has been carried out for the substances fluorescent-blue, phenosafranine, rhodamine, and Magdala-red in various solvents. In general it is shown that the more fluorescent a solution the more absorbent it is, but there is no strict relationship between the two quantities. The absence of a relationship is explained in the following way: Absorption of light in which the light energy is converted into heat has no influence on the fluorescence of a solution. Absorption of light in which the light is converted into waves of greater wave-length, that is, into fluorescent waves, has naturally an influence on fluorescence, and this absorption is proportional to the fluorescence. The absorption measured is the sum of these two quantities, and in consequence cannot be proportional to the intensity of the fluorescence. J. F. S.

Rotatory Power and Refractivity. II. The Rotatory Powers, Refractivities, and Molecular Solution Volumes of Camphor, Bromocamphor, and Ethyl Tartrate in Certain Solvents. DAVID HENRY PEACOCK (T., 1915, **107**, 1547—1567).—In continuation of previous work (T., 1914, **105**, 2782), an attempt

is made to connect together the rotation and the refractive index of a solution of an active substance in an inactive solvent by means of a relationship, $[\alpha]=\{(r'p^2a)/2\}(n^2-1)(n^2-1+1/a)$, where n is the refractive index, p is the frequency of the light used, and r' and a are constants. The rotation of camphor has been determined at 25° at various concentrations, in alcohol, acetone, ethyl acetate, benzene, chlorobenzene, and *iso*butyl alcohol; and of bromocamphor in alcohol, acetone, ethyl acetate, and benzene; and of ethyl tartrate in *n*- and in *iso*-butyl alcohol. For camphor and bromocamphor there is a parallelism between the values of $[\alpha]_D^{25}$ and the refractivity expression, $(n^2-1)(n^2-1+1/a)$, whilst the refractivity divided by the specific rotation gives an almost constant value. In the case of ethyl tartrate in *n*- and in *iso*-butyl alcohol there is no apparent connexion between the rotation and the refractivity.

T. S. Pa.

A Comparison of the Positive Rays with the Spectrum of the Positive Column in a Mixture of Hydrogen and Helium. Harold Smith (*Phil. Mag.*, 1915, [vi], **20**, 805—811).—The research is concerned with the question whether a gas, the spectrum of which is masked by another, continues to take part in the electrical convexion. Simultaneous photographs of the spectrum of the positive column and the lines of the positive rays were taken in mixtures of helium and hydrogen, varying from 30% to 2% of helium. The pressure, however, has to be kept so low to secure good positive ray photographs that the light of the positive column is extremely faint. As far as could be seen, the helium spectrum disappears at a much earlier stage than the helium positive rays, which are remarkably persistent, the helium line being still visible in mixtures containing too small a proportion of helium to be estimated. No simple connexion between the two phenomena was observed. It is suggested that the masking effect of one gas on the spectrum of another may be connected with the greater ability of the heavier atoms to acquire multiple charges, thus forming more strongly attractive centres, and consequent greater frequency of recombination with subsequent spectral emission. F. S.

The Action of Rays on Colloids. Walther Löb (*Biochem. Zeitsch.*, 1915, **71**, 479—480).—The author calls attention to the similarity between results obtained by himself and Sato (A., 1915, ii, 409) and those recently obtained by Fernau and Pauli (A., 1915, ii, 722). S. B. S.

The Variation of the Emanation Content of Certain Springs. R. R. Ramsey (*Phil. Mag.*, 1915, [vi], **30**, 815—818).—Two springs near Bloomington, Indiana, have been tested weekly for their content of radium emanation over a period of nine months. This was found to increase as the flow of the spring increased, maximum values being obtained in the wet season, which suggests that the emanation is dissolved as the water percolates through the soil, a larger amount being obtained when the process of percolation is rapid. F. S.

The Recoil of Radium-*D* from Radium-*C*. A. B. WOOD and W. MAKOWER (*Phil. Mag.*, 1915, [vi], **30**, 811—815).—The active deposit of 300 millicuries of radium emanation was concentrated on a wire 0·14 mm. diameter and 1 cm. long, and mounted in the apparatus previously used by Walmsley and Makower in experiments on the recoil of radium-*B* from radium-*A* (A., 1915, ii, 79). The magnetic field was not excited until eight minutes after the wire had been mounted, to allow radium-*A* to decay. Then the magnetic field was excited for seventy-five minutes. A Schumann plate was used in the hope that a direct action of the recoiling particles on the plate might be observed, previous failure to obtain a direct action being probably due to the large mass of gelatin in ordinary plates stopping the very feebly penetrating recoil particles. Between the traces of the deflected and undeflected α-rays, due mainly to radium-*C* and -*A* respectively, a faint line, which is attributed to the recoil stream of radium-*D*, was observed. Since the latter gives no α-rays and has a long period of transformation, no photographic action from its own rays or those of a subsequent product is to be expected. The line was not exactly midway between the α-ray lines, which is attributed to the radium-*C*, the source of the particles, itself being formed from radium-*A*, having been driven some distance below the surface of the wire by previous recoils. The conclusion reached is that radium-*D* is projected with a single positive charge, as when radium-*B* recoils from radium-*A* (*loc. cit.*). No general conclusion is possible from this, since the elements compared are isotopic. Possibly in other cases recoil atoms may carry multiple charges, but unfortunately it is difficult to put them to experimental test. F. S.

The Constitution of Radioactive Atoms. HEINRICH RAUSCH VON TRAUBENBERG (*Chem. Zentr.*, 1915, ii, 382—383; from *Nach. K. Ges. Wiss. Göttingen*, 1915, 28—34).—By applying the laws of mechanics and making certain assumptions, Debye has been able to conceive a stable model of the hydrogen molecule and atom with the aid of which the dispersion and specific heat of this element could be calculated, the results according well with those of direct experiment. Proceeding in a similar manner with radioactive atoms, the author has been able to arrive at a conception from which it is possible to deduce certain quantitative relationships; thus with the β-rays a satisfactory quantitative agreement is found between the deduced results and the direct experimental facts, whilst with the α-rays the agreement between the two sets of results is only approximate. D. F. T.

The Conduction of the Electric Current in Ethyl Ether. JOSEPH FASSBINDER (*Ann. Physik*, 1915, [iv], **48**, 449—480).—The electrical conductance of ethyl ether is mainly due to the presence of traces of foreign substances which are adsorbed by the electrodes and resolved into ions. Some of these ions are much more readily detached from the electrodes than others. For this reason

the current increases with the strength of the electrical field. It is independent of the distance between the electrodes, but varies largely according to the nature of the impurities in the ether. A considerable difference is shown in the conductance phenomena when platinum electrodes are replaced by electrodes of silver. The substances which give rise to the ions are only slightly adsorbed by platinum, and the ions formed are readily removed. This is in agreement with the fact that the strength of the current diminishes rapidly with time. On the other hand, silver electrodes show a much greater adsorption capacity, and the ions are not nearly so easily removed. The conductance shows, therefore, little change when a current is passed for some time.

The saturation current observed with platinum electrodes (Schröder, A., 1909, ii, 462) represents the stationary condition which is ultimately attained on the continual passage of the current. In this condition the rate of production of ions is equal to the rate of removal.

Pure ethyl ether has a very small conductivity. The values hitherto recorded are very largely due to impurities. H. M. D.

Potentials of Calomel and Hydrogen Electrodes. N. EDWARD LOOMIS (*J. Physical Chem.*, 1915, **19**, 660—664).—A general discussion on the potential of the electrodes $Hg|HgCl.N/10KCl$ and $H_2/0{\cdot}1NHCl$. After considering results based on the measurement of the hydrolysis of aniline hydrochloride, and on the degree of ionisation of acetic acid ($0{\cdot}25N$), it is decided that the potential of the former electrode lies between 0·337 and 0·336 volt, and is probably nearer the latter than the former figure.

J. F. S.

Passivity of Metals. N. A. IZGARYSCHEV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1337—1373. Compare A., 1913, ii, 664).—The author has investigated the polarisation of various electrodes in presence of methyl or ethyl alcohol, the conclusions drawn from the results obtained being as follows.

Although chemical polarisation does not occur with cadmium, zinc, copper, silver, etc., immersed in aqueous solutions of their salts, this phenomenon is exhibited to a marked degree on addition of an alcohol; in the case of nickel, however, the degree of polarisation is not only not increased by addition of methyl alcohol, but is even strongly diminished in 100% methyl alcohol. It is highly probable that one of the causes of the polarisation in such cases is the slowness with which the electrode processes take place. Since the composition of the solvent exerts such an important influence on the velocity of the electrode processes, a less probable explanation of the phenomena observed is furnished by the hypothesis that the cathodic polarisation depends on the slowness of discharge of the ions at the electrode, and is therefore an electronic process.

The course of ionisation in solution may be explained on the basis of two hypotheses, the first of which assumes that in solutions of metallic salts which are not too dilute complex ions are

formed without the participation of the solvent. Thus, copper sulphate in water would ionise according to the scheme (compare Abegg and Labendzinski, A., 1904, ii, 241) $2CuSO_4 \rightleftarrows Cu^{\cdot\cdot} + [Cu(SO_4)_2]''$ and $2CuSO_4 \rightleftarrows (Cu_2SO_4)^{\cdot\cdot} + SO_4''$. The character of the processes at the electrodes would thus depend entirely on the velocities of formation and distribution of such complexes. This hypothesis is justified in its application to many of the phenomena of aqueous solutions, but is inapplicable to the explanation of the cases of polarisation now considered, since the participation of the solvent must be regarded as completely proved. The second hypothesis assumes the course followed by the electrode processes to be determined by the speeds of formation and of decomposition of solvate compounds in the formation of which either the alcohol and the water together or the alcohol alone take part.

The phenomena of passivity, that is, the polarisation of the electrodes on electrolysis and the passivification of the equilibrium potentials of the same metals, are not in direct interdependence. It is found, indeed, that metals which are strongly polarised on electrolysis sometimes give active potentials. The latter are rendered passive principally as the result of the formation, under the influence of coupled oxidising processes, on the surface of the electrodes of a coating of oxide compounds, which probably include molecules of the solvent in their composition. T. H. P.

Hydrogen and Hydroxyl Ion Activities of Solutions of Hydrochloric Acid, and of Sodium and Potassium Hydroxides in the Presence of Neutral Salts. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1915, **37**, 2460—2482).—The *E.M.F.* of cells of the type

$$Hg \mid HgCl \mid N\text{-}KCl \mid \text{sat } KCl \mid HCl(0{\cdot}1N),MX \mid H_2,$$

has been measured with the object of determining the influence of the neutral salt MX on the hydrogen ion concentration. The neutral salts used were potassium chloride, sodium chloride, barium chloride, strontium chloride, calcium chloride, lithium chloride, and sodium bromide. A series of measurements was also made in which MX was replaced by mannitol. A similar series of measurements was made with cells of the type

$$Hg \mid HgCl \mid N\text{-}KCl \mid \text{sat } KCl \mid NaOH(0{\cdot}1N),MX \mid H_2$$
$$Hg \mid HgCl \mid N\text{-}KCl \mid \text{sat } KCl \mid KOH(0{\cdot}1N),MX \mid H_2$$

and in these cases the neutral salt MX was potassium chloride, sodium chloride, or lithium chloride.

It is shown that the hydrogen ion activity and concentration in $0{\cdot}1N$-hydrochloric acid solution are increased by the addition of the above-mentioned neutral salts. The hydroxyl ion activity and concentration in $0{\cdot}1N$-solutions of sodium and potassium hydroxide solutions are also increased. In the case of hydrochloric acid, the increase in activity does not vary much with the different salts, but in the case of sodium and potassium hydroxides this is not the case. The fact that sodium bromide produces the same effect on

the hydrogen ion activity of hydrochloric acid solutions as does sodium chloride has been shown to be in accord with the law of mass action. A solution of 0·1N-hydrochloric acid has its hydrogen ion concentration increased from 0·092 to 0·1765 by the presence of 3N-potassium chloride. This points to the conclusion that the solution acts as though it were contracting or that the volume of the solution has decreased. J. F. S.

Galvanic Cells of Lead Isotopes. G. VON HEVESY and F. PANETH (*Monatsh.*, 1915, **36**, 795—803).—The *E.M.F.* of cells of the following composition has been investigated:

i. (Pt) | PbO_2 | Ra-$G(NO_3)_2$,HNO_3,Ra-GO_2 | Comparison electrode.
ii. (Pt) | Ra-GO_2 | $Pb(NO_3)_2 10^{-3}N$,HNO_3,$10^{-3}N$,PbO_2(sat) | Comparison electrode.
iii. (Pt) | Ra-GO_2 | Ra-$G(NO_3)_2 10^{-3}N$,HNO_3,$10^{-3}N$,Ra-GO_2(sat) | Comparison electrode.

It is shown from the results that lead nitrate may be substituted by an equally concentrated solution of radium-G nitrate without changing the *E.M.F.* of a cell of the type $PbO_2|Pb(NO_3)_2|$comparison electrode by more than 10 micro-volts. Consequently, it follows that radium-G and lead are electrochemically interchangeable to within the limits of the experimental error.

The cell

(Pt) | PbO_2 | $Pb(NO_3)_2 10^{-3}N$,$HNO_3 10^{-3}N$,PbO_2(sat) |
Ra-$G(NO_3)_2 10^{-3}N$,$HNO_3 10^{-3}N$,Ra-GO_2(sat) | Ra-GO_2 | (Pt),

was also investigated, and shown to have an *E.M.F.* of about 10 micro-volts. This experiment shows the similarity, to within this figure, of the electrode potentials of lead and radium-G. In the above cell it has been assumed that the liquid contact potentials are negligible. Direct experiments to measure the value of the contact potential $Pb(NO_3)_2|$Ra-$G(NO_3)_2$ show that its value is less than 1 micro-volt. J. F. S.

Uranous-uranyl Photo-electric Cells. G. TRÜMPLER (*Zeitsch. physikal Chem.*, 1915, **90**, 385—457).—The single potentials of the elements $Pt/U^{IV}/U^{VI}$ have been measured for solutions of various concentrations with both illuminated and dark electrodes. The platinum electrodes were both platinised and bright. The measurements were made by the compensation method, whilst a current of $5{\cdot}4 \times 10^{-9}$ amperes was drawn from the cells. It is shown that such photo-electric elements behave in the same way as ordinary elements when current is withdrawn, and that the Becquerel effect observed is due to the uranyl salt. In these cases the Becquerel effect is the result of a volume effect of the light in the uranium salt solution. The displacement of the potential in light is dependent on the chemical condition of the electrode, that is, it depends on the nature of the potential in the absence of light. There is no reversible displacement of the potential in light of a system $U^{VI} + 2A^n = U^{IV} + 2A^{n+1}$, although many substances (A) or their ions are capable of exerting strong influence on the displace-

ment of the potential in light, of the nature that these displacements are decreased by small quantities of these substances, and under some conditions they even change the sign of the potential. There are, consequently, systems with negative and positive effects depending on the composition of the system. The negative effect is weakened by the presence of iodine, hydriodic acid, vanadium sulphate, vanadyl sulphate, hydrochloric acid, ferric sulphate, and ferrous sulphate. The positive effect is weakened by the presence of sulphur dioxide, uranous sulphate, and oxalic acid. All the substances which have a weakening action on the positive or negative Becquerel effect also reduce the fluorescence of uranyl sulphate solutions. The fluorescence of these solutions is also decreased by an increase in the temperature. The author evolves a theory to explain the Becquerel effect in uranium salts. The displacement of the potential is regarded as being due to variations in the dark potential which are brought about by the occurrence of reactions which produce other potentials. Thus the negative Becquerel effect is attributed to the formation of quinquevalent uranium and the negative effect to the presence of octavalent uranium in the illuminated region. Both these higher stages of oxidation are regarded as being formed by the action of light on the uranyl salt. Illuminated uranyl salts act in the same way as non-illuminated uranyl salts with other oxidisable and reducible substances, and these reactions occasion the observed weakening of the positive or negative Becquerel effect. Direct reversion of the uranyl ion, which has been illuminated, in the dark occurs with the emission of fluorescence. All chemical reactions of illuminated uranyl salts weaken the fluorescence. The oxidation of organic acids effected by uranyl salts is regarded as a special case of such reactions. J. F. S.

Thermo-electromotive Force of Certain Iron Alloys. T. S. FULLER (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 241—251).—Swedish iron is melted in an aluminium crucible with aluminothermic chromium and manganese, and commercially pure nickel and cobalt. The metals are melted in a vacuum or in hydrogen, and are well stirred and then allowed to cool in the crucible. The thermo-*E.M.F.* is measured against copper after the ingot has been forged and drawn down to wire. When the hot junction is at 100° and the cold at 0°, iron–nickel alloys with more than 5% of nickel are negative to copper, the curve showing a sharp cusp just above 90% of nickel. Iron–chromium alloys up to 30% of chromium are all positive. Iron–cobalt alloys become negative with 5% of chromium. Some ternary alloys of the iron–nickel–chromium and iron–nickel–manganese series have also been examined and plotted, but the data are very scanty. C. H. D.

Electro-deposition of Smooth, Solid Lead from Lead Nitrate Solutions. FRANK C. MATHERS and ASA MCKINNEY (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 131—140).—Lead is usually deposited from nitrate solutions as loose crystals. The addition of various

colloids has been tried, but in almost all cases without effect on the deposit. The gummy residue from Curaçao aloes, obtained in the manufacture of aloin, has been used with success in solutions of lead acetate, lactate, and formate (A., 1915, ii, 40), and is also found to have the required effect in nitrate solutions. The most suitable electrolyte contains 10% of lead nitrate, 2·5 to 5% of acetic acid, and 1% of aloes residue. When a current density of 0·4 ampere per sq. dcm. is used, the deposit is smooth and coherent. It is not possible to use nitric acid in place of acetic acid.

C. H. D.

Transport Number of Ferrous Ions in Solutions of Ferrous Chloride. (MME.) A. STEPNICZKA-MARINKOVIĆ (*Monatsh.*, 1915, **36**, 831—843).—The transport number of the ferrous ion in solutions of ferrous chloride has been determined for the concentrations 0·988*N*, 0·494*N*, and 0·172*N*. The solutions contained hydrochloric acid of various concentrations for the purpose of repressing hydrolysis. The following values are found for the solutions respectively: $0·300 \pm 0·003$, $0·326 \pm 0·005$, and $0·375 \pm 0·006$. The transport number for infinite dilution is extrapolated and found to be 0·414. The mobility of the ferrous ion is calculated to be 39 in the solution 0·172*N* and 46 in a solution of infinite dilution. From these figures it is shown that the hydration of the ferrous ion is 60 molecules of water and that of the chlorine ion 21 molecules of water.

J. F. S.

Transport Number of the Ferric Ion in Ferric Chloride Solutions. K. HOPFGARTNER (*Monatsh.*, 1915, **36**, 751—769).—The transport number of the ferric ion has been determined in solutions of ferric chloride of concentrations 1·242*N*, 0·444*N*, and 0·137*N*. The solutions contained hydrochloric acid of various concentrations, which was added for the purpose of repressing the hydrolysis. The following mean values have been obtained: $0·292 \pm 0·004$, $0·359 \pm 0·003$, and $0·384 \pm 0·003$ for the three concentrations respectively. From these values the value for infinite dilution is extrapolated and found to be 0·396. The mobility calculated from the above data at 18° is found to be approximately 43, a value somewhat smaller than the value found by Marinkovič (preceding abstract) for the ferrous ion. This relationship between the mobilities of the two ions is in accord with Hevesy's theory (*Jahrb. Radioaktiv Elektronik*, 1914, **11**, 419). Calculations of the amount of hydration of the ions by Riesenfeld's formula show that the ferric ion is less hydrated than the ferrous ion. From this result it is deduced that either the hydration alone is not determinative of the mobility, or the experimental conditions of the present work render the Riesenfeld formula inapplicable in the present case.

J. F. S.

Magneto-chemistry of Internally Complex Compounds. J. LIFSCHITZ and ERNST ROSENBOHM (*Zeitsch. Elektrochem.*, 1915, **21**, 499—501).—A number of examples of substances in which sub-

sidiary valencies are active are quoted to show that the determination of the magnetic susceptibility of these substances furnishes a ready means of detecting the activity of subsidiary valencies. The following types of substances are shown to have susceptibilities which are very different for the various isomerides: chromo-isomerides, conjugated alkali and alkaline earth salts, and non-electrolytes, such as the aminocrotonic esters. It is shown that the magnetic method of deciding structure in cases of this kind is superior to the absorption spectrum and conductivity methods, since the measurements can be effected with the solid substances, and the disturbing influence of the solvent is consequently avoided.

J. F. S.

The Thermal Conductivity of Refractories. BOYD DUDLEY (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 285—337).—The conductivity is measured by heating one side of a wall built up of the material to be tested, a water calorimeter being in contact with the opposite face. The temperature of the heated face is determined by means of thermo-couples, and the flow of heat by regulating the flow of water through the calorimeter and measuring the rise of temperature. Magnesite brick has about three times the conductivity of silica brick at 1000°. The surface drop of temperature, which is of importance in some furnaces, is neglected in this method of experiment. C. H. D.

Specific Heat at Low Temperatures. II. Specific Heat of Copper between 14° and 90° (Absolute). W. H. KEESOM and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 484—493. Compare A., 1915, ii, 83).—In consequence of improvements in the experimental arrangement, further measurements have been made of the specific heat of copper at low temperatures. The atomic heat rises from 0·0396 at a mean temperature of 14·51° to 0·1155 at 20·19° (mean), 0·234 at 25·37° (mean), and 0·870 at 40·22° (mean). When compared with the atomic heat values calculated from the equation $C_v = kT^3$ it is found that the atomic heat decreases with falling temperature more rapidly than it should do according to Debye's law. H. M. D.

Dulong and Petit's Law. STEFANO PAGLIANI (*Gazzetta*, 1915, **45**, ii, 317—327).—On the basis of either the Maxwell-Boltzmann kinetic theory of specific heat or Einstein's formula for the atomic heat, the author shows that the temperatures at which different elements begin to diverge from Dulong and Petit's law fall as the atomic coefficients increase, and that, in general, the temperatures at which elements exhibit the same atomic heat fall as the coefficients become larger. At low temperatures, where the specific heats are small, the values of the atomic heats of the various elements at one and the same temperature tend to increase with the atomic coefficients, that is, with the number of negative electrons. This is, however, not the case at other temperatures, for instance, at those near the temperature at which Dulong and

Petit's law holds. The atomic heat varies only between 0 and 9, and for lead, with the high atomic coefficient 207, its maximum value is 7·4, whilst for lithium, with the atomic coefficient 7, it scarcely reaches 7. These facts confirm the conclusion, deduced from the laws of dispersion, that the free electrons do not contribute to the specific heat.

These results and those obtained previously (A., 1913, ii, 101) render increasingly evident the influence exerted on the physical properties of substances by the relative magnitudes of the masses of their atoms. T. H. P.

Isothermals of Diatomic Substances and their Binary Mixtures. XVIII. The Isothermal of Hydrogen at 20° from 60 to 100 Atmospheres. H. KAMERLINGH ONNES, C. A. CROMMELIN, and (MISS) E. I. SMID (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 465—472. Compare A., 1915, ii, 143).—Measurements of the pressure-volume relations of hydrogen at 20° have shown that the value of pv can be represented very accurately by the equation $pv = 1{\cdot}07261 + 0{\cdot}0^3 65712D + 0{\cdot}0^5 12926D^2$. Whereas the coefficient in the second term of this equation agrees quite well with the value expected on the basis of previous observations, the coefficient in the third term is much larger than would be anticipated by reference to earlier measurements. H. M. D.

Isothermals of Monatomic Gases and of their Binary Mixtures. XVII. Isothermals of Neon and Preliminary Determinations Concerning the Liquid Condition of Neon. H. KAMERLINGH ONNES and C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 515—520).—The isothermals of neon have been measured over a considerable range of pressure at 20° and 0°, and over a small range of pressure at −182·6°, −200·1°, −208·1°, −213·1°, and −217·5°. For 20°, $pv = 1{\cdot}0731 + 0{\cdot}0^3 51578D + 0{\cdot}0^6 82778D^2$, and for 0° $pv = 0{\cdot}99986 + 0{\cdot}0^3 41334D + 0{\cdot}0^5 11538D^2$. The vapour pressure of liquid neon increases from 32·35 cm. at −248·67° (the triple point) to 81·62 cm. at −245·68°. The boiling point is −245·92°. D = 1·204 at −245·88°, 1·248 at −248·51°.

By a method involving a comparison of the isothermals with those of other gases, a preliminary estimate of the critical temperature has been made. The comparison with hydrogen and with oxygen gives $\theta_k = -231°$, and that with argon −228°. H. M. D.

Experiments with Liquid Helium. The Measurement of very Low Temperatures. XXV. Determination of the Temperatures which are obtained with Liquid Helium, especially in Connexion with Measurements of the Vapour Pressure of Helium. H. KAMERLINGH ONNES and SOPHUS WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 493 - 507).—Helium thermometers suitable for the measurement of the lowest attainable temperatures are described, and the correction to be applied for thermal molecular pressure is discussed. The thermometers have been made use of in the measurement of the vapour pressure of

liquid helium with the following results: $t=1\cdot475^{\circ}$ (absolute), $p=0\cdot415$ cm.; $3\cdot516^{\circ}$, $35\cdot95$; $4\cdot205^{\circ}$, $75\cdot75$; $4\cdot90^{\circ}$, $132\cdot9$; $5\cdot16^{\circ}$, $166\cdot8$. The interpolation formula $\log p=3\cdot7290-7\cdot978/T-0\cdot13628/T^2+4\cdot3634/T^3$ represents the results moderately well. It was not found possible to bring the data into agreement with Nernst's vapour-pressure formula. H. M. D.

Methods and Apparatus used in the Cryogenic Laboratory. XVI. The Neon Cycle. H. KAMERLINGH ONNES (*Proc. K. Acad. Wetensch. Amsterdam*, 1915, **18**, 507—515).—Temperatures between 14° and 20° (absolute) are readily attained by means of liquid hydrogen, between 55° and 90° by means of liquid oxygen. The intermediate range (20—55°) is of great importance in connexion with low temperature work, and a form of apparatus, consisting of liquefier and cryostat, is described, by means of which temperatures between 20° and 27° can be produced by the use of liquid helium. By the use of a pressure-cryostat it is probable that the liquid helium range of temperature can be extended up to 34° (absolute). H. M. D.

Molecular Attraction. XII. J. E. MILLS (*J. Physical Chem.*, 1915, **19**, 650—659. Compare A., 1915, ii, 315, and earlier papers).—A theoretical paper, in which it is shown that the persistent exact, or very approximate, truth of the relationship $dP/P=dT/T$ in many circumstances suggests that the relation may be always true for constant volume and for phase change equilibrium conditions, that is, in the case where P indicates the numerical sum of the internal and external pressures. A general discussion is entered into concerning deductions made in previous papers. The following new relationship is derived: The amount of energy retained by a system of n particles forming a stable system under the action of the molecular attractive force is equal to the amount of energy given out by these particles in coming into the system from an infinite distance. This relationship is affected by temperature in a manner not yet understood. J. F. S.

Vapour Pressure of Thallium Amalgams. JOEL H. HILDEBRAND and ERMON DWIGHT EASTMAN (*J. Amer. Chem. Soc.*, 1915, **37**, 2452—2459).—A series of vapour-pressure determinations of thallium amalgams has been carried out at temperatures from 329° to 324°. The composition of the amalgams varied from 1·673 parts of thallium to 36·408 parts of mercury to 7·221 of thallium to 1·796 parts of mercury, that is, from 22·1 to 0·253 molecules of mercury to 1 molecule of thallium. The method of determination is the same as that previously adopted in the case of bismuth amalgams (A., 1914, ii, 800). It is shown that the relative vapour pressures of the amalgams are always less than those calculated by the Raoult law. The existence of the compound $TlHg_2$ is discussed in connexion with the vapour-pressure measurements and also in connexion with *E.M.F.* measurements of thallium amalgams previously published (A., 1910, ii, 384) by Richards and Wilson. J. F. S.

The Heats of Equilibrium and the Law of Saturated Solutions. ALBERT COLSON (*Compt. rend.*, 1915, **161**, 586—589).—The author has determined the molecular heats of addition, λ, for some four salts, and in the case of sodium chloride has made the determinations over a range of temperatures. The difference between the molecular heat of saturation, L, and the molecular heat of addition, λ, gives the molecular heat of equilibrium, ρ, at the given temperature. The values obtained are:

	λ (cal.).	L (cal.).	ρ (cal.).	Temp.
Sodium chloride............	−153	−448	−295	21·5°
Potassium nitrate	−1257	−7145	−5888	13·5°
Potassium chloride.........	−740	−4082	−3342	6·5°
Ammonium chloride	−128	−3576	−3446	23·0°

In the case of sodium chloride the variations with temperature are:

T	31·5°	27·6°	21·5°	17·4°	13·5°	6·85°	0°
λ (cal.)...	0	−62·2	−153	−221·4	−296	−388	−501
ρ (cal.)...	—	—	−293	—	—	− 85	+16

The heat of equilibrium thus changes sign at a temperature near 0°. Since there is no correlative variation in the solubility of sodium chloride, this is an indication that the formula $i.dC/C=500\rho dT/T^2$, governing the heat of equilibrium, is not in agreement with the experimental results for sodium chloride.

W. G.

Volume and Heat. G. A. HAGEMANN (*Zeitsch. Elektrochem.*, 1915, **21**, 493—495).—A theoretical paper, in which the author, reasoning from volume and heat changes which occur in (1) the formation of calcium hydride, (2) water, and (3) hydrogen peroxide, deduces that there is an exact connexion between the volume of the atom and its energy. It is shown that in calcium hydride the hydrogen atom has decreased so much in volume owing to its loss of energy in the formation of this compound that it has become small enough to exist in the volume of the calcium atom. The state of aggregation of water is held to be due to a considerable energy exchange, and the oxygen in hydrogen peroxide is present as ozone. J. F. S.

Determination of the Affinity of the Reaction: $KClO_3 + NaI = KI + NaClO_3$. E. GÜNTELBERG (*K. Danske Videnskab, Selskab. Forhand.*, 1915, Nos. 3—4, 241—254).—A continuation of the work of Brönsted on the affinity of chemical processes (A., 1913, ii, 295). It is shown that the affinity of the double decomposition $KClO_3 + NaI = KI + NaClO_3$ can be determined from a knowledge of the vapour pressure (p_1) at the transformation temperature of the system containing all four salts in equilibrium with the saturated solution, and of the vapour pressure (p_2) of the system $NaI,2H_2O + NaI$ at the same temperature, the affinity (A) being given by the expression $A = 2RT \log_e (p_1/p_2)$.

By dilatometric and other methods the transformation tempera-

ture was found to be 29·80°. The vapour pressures were measured in a special apparatus, and found to be $p_1 = 9·52$ and $p_2 = 3·59$ cm. of bromonaphthalene, from which the affinity of the above reaction is calculated to be 1170 cal. (at 30°). It is calculated that the affinity at 100° will then be 1070 cal., which is in good agreement with Brönsted's value of 1050 cal. T. S. P.

[Electrical] Conductivity and Viscosity of Some Rubidium and Ammonium Salts in Ternary Mixtures of Glycerol, Acetone, and Water at 15°, 25°, and 35°. P. B. DAVIS, W. S. PUTNAM, and HARRY C. JONES (*Zeitsch. physikal. Chem.*, 1915, **90**, 481—509).—The viscosity and electrical conductivity of solutions of ammonium and rubidium bromides and iodides have been determined at a series of concentrations in ternary mixtures of glycerol, acetone, and water of various compositions. From the viscosity values the fluidity and temperature-coefficient have been calculated. The temperature-coefficient of the electrical conductivity has also been calculated. The conductivity values indicate that water and acetone act as dissociating media toward glycerol. The decrease of the dissociation of an associated liquid by another liquid in a ternary mixture is much greater than in a binary mixture, and this occasions a decrease in the values of the conductivity and viscosity. Consideration of the fluidity of glycerol, acetone, and water in connexion with the hypotheses of Dutoit and Aston and of Thompson and Nernst, offers an explanation of the difference between the conductivity and fluidity curves of the ternary mixtures. The temperature-coefficients of the fluidity are larger than those of the conductivity, as in the case of binary mixtures. The difference is probably due to the formation of solvates. The minimum observed in many of the conductivity curves can be deduced from the fluidity of the solutions. A polymerisation of the salts by acetone possibly explains the changes in the fluidity which cause the minima in the conductivity and viscosity curves. The values of the conductivity and fluidity, of the solvents containing the largest quantity of glycerol, are smaller than those calculated from the mean, and more so than the corresponding values of any other mixture of these three substances. The temperature-coefficients of the conductivity agree approximately with those calculated. The fluidity is shown to be the most determinative factor in the conductivity value. J. F. S.

Viscosity of Ethyl Ether near the Critical Temperature. A. L. CLARK (*Trans. Roy. Soc. Canada*, 1915, **9**, 43—67).—The author has measured the damping effect on the oscillations of a gold cylinder suspended in ether in a sealed tube at different temperatures up to and above its critical temperature. The apparatus used consisted of two cylindrical vertical glass tubes connected near their top by a narrow glass tube, a golden cylinder being suspended in one limb. Into this apparatus carefully purified ether was distilled, the necessary precautions being taken to prevent the occlusion of air in the ether. An electrical heating

arrangement was used, capable of keeping the temperature constant over a range from 30° to 300°. Determinations were made of the logarithmic decrement with the cylinder immersed in the liquid for a number of temperatures up to and beyond the critical temperature, and then for falling temperatures down to the critical temperature again. The same thing was done with the cylinder immersed in the vapour. Changes with time were studied by maintaining the temperature constant within a few hundredths of a degree with the cylinder in the liquid at different temperatures near the critical temperature. The same observations were made with the cylinder in the vapour.

With the cylinder in the liquid side of the tube the logarithmic decrement of the oscillations decreases with rising temperature, reaching a minimum near the critical temperature and then rising rapidly with the temperature. With the cylinder in the vapour there is a steady rise in the decrement, which gradually becomes more rapid as the critical temperature is reached, and more rapid when it is passed. When the tube is maintained at constant temperature above and near the critical temperature the liquid side shows a decrease in the logarithmic decrement. The same is true for constant temperature below the critical temperature. On the vapour side under constant temperature there is first an increase and then a decrease in the decrement near the critical temperature. Above the critical temperature the decrement curve for falling temperatures is slightly below that for rising temperatures on the vapour side. The difference is very slight.

The results obtained may be partly explained on the grounds of diffusion of the denser part of the substance from the liquid side to the vapour side. This difference in density between the two sides may be equalised by heating to a much higher temperature or by maintaining at constant temperature near the critical temperature for a long time. Diffusion alone does not appear, however, to account for all the changes found. There are apparently real changes in the nature of the substance near the critical temperature, these changes being slow, and equilibrium only being reached after a considerable lapse of time. In explaining these changes, which he finds to be most decided at 194°, the author is inclined to agree with the views of Traube (A., 1902, ii, 537) and de Heen as to the existence of liquid molecules and vapour molecules, the former being congeries of the latter, and producing them by disintegration. W. G.

Adsorption. XII. Principle of the Mobility of Water in Adsorption Compounds. A. V. Rakovski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1326—1329. Compare A., 1915, ii, 235).—After filtration, ferric, chromium, and aluminium hydroxides contain about 90—95% of water, most of which evaporates at constant rate under constant external conditions. As drying proceeds, these gels develop many cracks, which greatly increase the surface, but do not affect the rapidity with which the evaporation of the water proceeds. This fact is explained by the very marked mobility of

water in gels, which are adsorption compounds (compare van Bemmelen, "Die Absorption," 1910; Löwenstein, A., 1909, ii, 736). In order to contrast this mobility with the far lower one of water in an ordinary solution, the author has exposed (1) moist potato starch, and (2) aqueous sulphuric acid of vapour pressure 15 mm. at 19°, in desiccators in which the pressure of aqueous vapour was maintained at 9, 11, 9, etc., mm. during successive periods of twenty-four hours, the temperature being 19° throughout. The course followed by the change in the water-content in each case is in accord with the theoretical deductions of Duhem (A., 1900, ii, 338). T. H. P.

The Effects of Certain Electrolytes and Lipoid Solvents on the Osmotic Pressures and Viscosities of Lecithin Suspensions. ADRIAN THOMAS (*J. Biol. Chem.*, 1915, **23**, 359—376).—The osmotic pressure of lecithin emulsions was measured in celloidin bags by Lillie's method in the presence of various electrolytes. The pressures indicated were small. Electrolytes decrease the osmotic pressure in the following order, the first-named having the greatest effect: hydrogen chloride, sodium iodide, sodium bromide, sodium chloride, sodium hydroxide. Electrolytes also decrease the viscosity of lecithin suspensions. Lipoid solvents, on the other hand, generally increase both the osmotic pressure and viscosity. S. B. S.

Colloidal Clay. PAUL EHRENBERG and GUY GIVEN (*Kolloid Zeitsch.*, 1915, **17**, 33—37).—Experiments are described which are said to support the view that clay gives a true colloidal solution in contact with water. Centrifuging for half an hour at the rate of 2000 revolutions a minute produced no appreciable segregation. Ultramicroscopic measurements showed that the average diameter of the colloidal particles was about 140 $\mu\mu$. H. M. D.

Vapour Pressure of Gelatin–Water Mixtures. KURT GERIKE (*Kolloid Zeitsch.*, 1915, **17**, 78—104).—Comparative measurements have been made of the vapour pressures of water and of gelatin–water mixtures in sol and gel form. The sols were examined by the short barometer tube method, and to get over the difficulties associated with local changes at the surface of the gels, a kinetic method has been worked out, in which the gels were subjected to the action of a current of air containing known quantities of water-vapour, and from the observed changes in the gels the equilibrium partial pressure could be derived.

The gelation sols have a slightly lower vapour pressure than pure water. The difference is very small, and increases very slightly with increasing concentration of the gelatin in the sol. The vapour pressure of solutions of potassium bromide is increased on the addition of gelatin. In these circumstances sodium chloride solutions show a diminution in the vapour pressure, whilst lithium chloride and ammonium nitrate solutions show an effect which varies according to the temperature.

Gelatin gels show a slight lowering of the vapour pressure as

compared with pure water, and the concentration of the gel is of little importance below 70% of gelatin. For gels containing more than this the vapour pressure is much lower, and there appears to be a further jump in the vapour-pressure curve when the concentration of the gelatin reaches about 94%.

Experiments are also described which have a close connexion with the observation made by von Schroeder (A., 1903, ii, 721) that gelatin which has taken up a maximum amount of water by direct contact with the liquid gives off a relatively large proportion of this when it is exposed to the saturated vapour at the same temperature. Cellulose (blotting-paper) when treated in the same manner takes up a further quantity of water in contact with the saturated vapour. If, however, the cellulose is dissolved in ammoniacal cupric oxide and reprecipitated, it behaves like gelatin. Conversely, when the surface of gelatin (after swelling in water) is roughened, it is found that it loses water much less readily on contact with saturated water-vapour. These observations show that the nature of the surface of the swollen protein has considerable influence on its behaviour in an atmosphere of water-vapour.

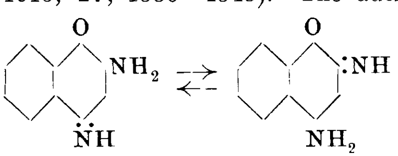
It is suggested that the swollen gel is under the influence of external pressure, which causes water to exude at the surface when the gel is suspended in the vapour. If the surface is smooth, then small drops of water are formed, which evaporate, but if the surface is rough, then the exuded water is distributed in the system of capillary depressions, and in these circumstances evaporation does not take place in the saturated vapour. H. M. D.

Non-, Uni-, and Bi-variant Equilibria. II F. A. H. Schreinemakers (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 531—542. Compare A., 1915, ii, 619).—A further theoretical discussion of various types of pressure-temperature diagrams, in which it is shown that these may be divided into three groups. The equilibrium in the system $KCl,CuCl_2,H_2O$ is examined in detail from the point of view of this subdivision of ternary systems. H. M. D.

The So-called "Lever Law" in the Theory of Phases and in Metallography, and an Italian Work of 1788. G. Bruni (*Gazzetta*, 1915, **45**, ii, 180—186).—What is virtually the "lever law" of metallography was published in a paper read by P. Barca before the Accademia di Scienze e Lettere in Padova in 1788.

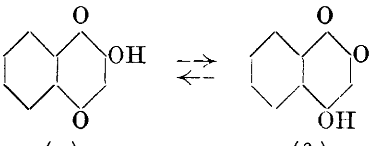
T. H. P.

Thermo-isomerisation of Naphthalinic Acid [1:2:4-Hydroxynaphthaquinone]. VI. O. Miller (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1536—1543).—The author's previous results (A., 1913, i, 877) showed that the dependency of the transformation (annexed formula) on the temperature is expressed by the linear formula $a(T-T^1)$, where a is a coefficient independent of the temperature but varying with the concentration,



T is the temperature of the experiment, and T^1 the lower temperature of the transformation. Similar investigations have now been made on the interconversion of α- and β-hydroxynaphthaquinones (annexed formula).

The hydroxynaphthaquinone was first converted, at the three temperatures 20°, 40°, and 94°, through the ammonium derivative into the three silver derivatives. The latter are of identical composition, but are respectively pale red, reddish-brown, and dark brown, and as the yield of α-compound increases with rise of temperature, it follows that the α-salt is darker than the β-salt. These silver compounds were then converted separately into the ethyl derivatives by treatment with ethyl iodide, and the α- and β-derivatives separated and estimated in each case. The results, calculated for 71·17 grams of the hydroxynaphthaquinone, which corresponds with 100 grams of di-iminonaphthol (*loc. cit.*), are as follows:



(α.) (β.)

Temp.	α-Ether.	β-Ether.	$\alpha+\beta$-Ethers.	Calculated total.
20°	6·44	76·19	82·63	82·71
40°	12·21	70·22	82·43	—
94°	28·37	53·58	81·95	—

These values are in linear dependence on the temperature. If the original neutralisation of the hydroxynaphthaquinone with ammonia is carried out in 95% alcoholic instead of in aqueous solution, the yields of the α- and β-ethers at 20° are changed from 6·44 and 76·19 respectively to 17·40 and 65·21 respectively. T. H. P.

Influence of Concentration on Isomerisation. VII. O. Miller (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1544—1549. Compare preceding abstract).—According to Ostwald ("Lehrbuch allg. Chemie," 2nd ed., 604), the equilibrium relations of two tautomeric forms in any solvent depend on the nature of the latter and on the temperature, but not on the dilution. The accuracy of this theoretical conclusion is, however, disproved by a number of examples (compare Wislicenus, A., 1896, i, 552; Miller, A., 1911, i, 308; Hantzsch, A., 1910, i, 811). In order to explain this apparent discord, the author makes use of the analogy between gaseous molecules and those in dilute solution in a solvent. The conclusion is arrived at that isomerisation is related inversely to the coefficient a of van der Waals's equation: when the gravitational attraction between similar molecules is great, the isomerisation will be slight, and vice versa. Further, since a increases with the concentration, the relation between isomerisation, J, and the concentration, K, will be $J=1/K^n$. The case of the transformation of amino-α-naphthaquinoneimide hydrochloride into 2-amino-α-naphthaquinone and 4-amino-β-naphthaquinone (compare A., 1911, i, 308) is considered. The following table shows the relation at 66° between the concentration of the original hydrochloride in grams per 100

grams of water and the amount of 2-amino-α-naphthaquinone formed per 100 grams of the hydrochloride:

Concentration of the hydrochloride.	Grams of 2-amino-α-naphthaquinone.	$a+bx$.
4	12·19	$8{\cdot}94+3{\cdot}16\times1=12{\cdot}10$
2	15·22	$8{\cdot}94+3{\cdot}16\times2=15{\cdot}26$
1	18·30	$8{\cdot}94+3{\cdot}16\times3=18{\cdot}42$
0·5	21·38	$8{\cdot}94+3{\cdot}16\times4=21{\cdot}58$

The values in the last column show that the yield of 2-amino-α-naphthaquinone increases in arithmetical progression as the concentration of the amino-α-naphthaquinoneimide hydrochloride diminishes in geometrical progression. Since the total yield of the two aminonaphthaquinones is 70·75 grams, it can be readily calculated that, when the concentration of the amino-α-naphthaquinoneimide hydrochloride at 66° is 1/65536 gram per 100 grams of water, the 2-amino-α-naphthaquinone alone is formed.

T. H. P.

Application of the Quantum Theory to Unimolecular Reactions. E. BUCH ANDERSEN (*K. Danske Videnskab. Selskab. Forhand.*, 1915, Nos. 3—4, 225—240).—The following assumption is made. In order that a molecule may enter into reaction with other molecules it must have a definite kinetic energy of its own; the distribution of the energy must be in accordance with Planck's law.

Using the above assumption, the author deduces an expression for the connexion between the velocity of reaction and the temperature in the case of unimolecular reactions, the expression containing the ordinary constants of the quantum theory. The expression is shown to be in agreement with the results of thermodynamics and with other deductions from the quantum theory. It was found to give a moderately good agreement between theory and experiment in the case of the hydrolysis of dibromosuccinic acid. T. S. P.

The Determination of the Concentration of Hydroxyl Ions. FRANCIS FRANCIS, FRANCIS HENRY GEAKE, and JAMES WILLIAM ROCHE (T., 1915, **107**, 1651—1673. Compare T., 1912, **101**, 2358; 1913, **103**, 1722).—The method employed for the measurement of the rate of decomposition of nitrosotriacetonamine under the catalytic influence of hydroxyl ions has been improved by operating at constant volume and measuring the pressure produced by the nitrogen evolved. The degree of accuracy attainable is appreciably greater than when the volume method is employed. Experiments have also been made with nitrosovinyl- and nitroso*iso*butyldiacetonamines. By the use of these substances, it has been possible to investigate hydroxyl ion concentrations between $0{\cdot}05N$ and $0{\cdot}35N$, a range which cannot be covered in experiments with nitrosotriacetonamine on account of the "drift" of the velocity coefficient.

For hydroxyl ion concentrations not exceeding $0{\cdot}15N$ when nitrosotriacetonamine is used, or $0{\cdot}4N$ in the case of the diacetou-

amines, the velocity coefficient is proportional to the hydroxyl ion concentration. At higher concentrations, the velocity reaches a maximum and then falls. For a given concentration of hydroxyl ions there is, moreover, a marked difference between the velocities observed when sodium and potassium hydroxides are employed as catalysts.

Neutral salts when added to dilute solutions of the alkali hydroxides reduce the catalytic activity to an extent which cannot be accounted for by the reduction in the ionisation of the bases. The data obtained with both potassium and sodium salts show that the influence of the added salts decreases in the series iodide, nitrate, bromide, chloride. In more concentrated solutions of the hydroxides, the relative influence of the nitrates becomes smaller. The neutral salt effect may be represented by the empirical equation $x/m=KC^{1/n}$, in which x is the reduction in the hydroxyl ion concentration produced by the addition of m mols. of salt per litre, C is the residual hydroxyl ion concentration, and K and n are constants.

The observations of the authors are not explainable on the assumption that the catalytic effect is the result of simultaneous changes in which the hydroxyl ion and the non-ionised hydroxides play the part of catalysts. The salt effects are also opposed to the view that the addition of salts increases the ionising power of the solvent medium. It is probable that the phenomena of catalysis in concentrated solutions of the alkali hydroxides are complicated by a "salt" effect which resembles that produced by the addition of neutral salts.

It seems possible that the reaction in concentrated solutions of alkali is determined by a preliminary combination between the base and the nitrosoamine, but no evidence in support of this view was obtained by conductivity measurements in dilute solutions of the hydroxides. H. M. D.

Passivification of Iron by Nitric Acid. S. W. YOUNG and ELTON MARION HOGG (*J. Physical Chem.*, 1915, **19**, 617—649).—An extensive series of determinations have been carried out at 0°, 10°, and 20° on the rate of solution of iron in nitric acid (D 1·025—1·400). A few isolated experiments were also made at higher temperatures and with various specimens of iron. It is shown that the value of the velocity-constant decreases with increasing concentration of acid throughout the whole range of concentrations. The decrease in the velocity is not uniform, but shows a rapid although not vertical drop in the velocity-constant at a concentration corresponding with D 1·260. In acids of D 1·260 or greater the velocity-constant shows a decrease as the time over which the solution has been proceeding increases, that is, the rate of solution is rapid at first and falls off as the reaction continues. This is interpreted as a gradual development of passivity, which increases as the reaction proceeds. At D 1·260 progressive passivification therefore commences, and a rapid drop in the velocity-constant occurs. This point in the velocity curves the authors

term the "passive break." The passive break falls a little from 0° to 10° and then rises continuously up to 100°. Passivifying acids, no matter how concentrated, bring about a slow but continuous solution of iron. It is shown that nitrogen tetroxide produces a passivity far greater than that produced by nitric acid when the dry gas is allowed to come into contact with the metal. This fact would seem to explain the facts that iron is only rendered passive by nitric acid which is either yellow or red in colour, whilst passive iron is rendered active by colourless nitric acid solutions. The general results seem to show that acids of such concentration that they yield nitrogen tetroxide when brought into contact with metals are capable of rendering metals passive, whilst those which do not evolve nitrogen tetroxide are unable to render metals passive, but rather render passive metals active. Acids of D 1·050 lose their power of rendering passive iron active after repeated use, presumably on account of an accumulation of nitrogen tetroxide or nitrous acid in the solution. When nitrogen tetroxide is bubbled through nitric acid in which iron is normally active, it has the effect of producing passivity. A similar effect is produced by the addition of nitrites. When iron is passivified in nitrogen tetroxide, a considerable and easily weighable amount of peroxide is absorbed by the iron. On exposure of such passive iron to moist air, drops of acid liquid are formed on the surface of the metal. It is stated that mere traces of nitrogen tetroxide are capable of rendering iron passive, since all iron articles in a room become passive if a little of the gas is allowed to escape into the air. Nitric acid of D 1·250 causes passivity at 10° and 20°, but not at 0°; this is probably to be explained by the non-formation of nitrogen tetroxide at this temperature. The more dilute the passivifying acid the more persistent the passivification produced. This is thought to be due to the greater depth of penetration of the nitrogen tetroxide owing to the longer time required for the passivification to be produced. From the experimental results it is deduced that the passive state is not a definite one, but that there are probably a number of degrees of passivity. The passive state seems to be the result of an equilibrium between iron and nitrogen tetroxide. Iron is capable of absorbing nitrogen tetroxide from any solution in which it is being produced, and the rate of reaction is thereby inhibited. The degree of inhibition will therefore be determined by the concentration of nitrogen tetroxide which it is itself capable of maintaining. Since iron passivified by dry nitrogen tetroxide is more persistently passive than that which is passivified in nitric acid, it seems probable that the amount of nitrogen tetroxide absorbed by iron from even very concentrated nitric acid is relatively quite small. The "passive break" is to be regarded as the point at which the reaction begins to develop relatively large amounts of nitrogen tetroxide. At concentrations below the "passive break" it seems probable that nitrogen tetroxide in decreasing amounts is still being developed, since the values for the velocity-constants continue to increase with dilution. The reason for the production of passivity by nitrogen tetroxide is not

entered into, but it is stated that there is no evidence of the production of a true gas film. J. F. S.

The Velocity of Solution of Liquids in Caoutchouc. PAUL BARY (*Compt. rend.*, 1915, **161**, 589—591).—Using the values obtained by Flusin for the swelling of vulcanised rubber by different liquids (compare A., 1908, ii, 359) the author shows that these results can be correctly represented by the formula $p=tp_s/(A+t)$, where t is the time in minutes, p_s the value of p for saturation, A a constant depending on the liquid and the experimental conditions, and p the weight of liquid absorbed in unit weight of solution. The values of A and p_s calculated for seventeen different liquids are tabulated, and it is found that the velocity of solution is given by the formula $v=B(p_s-p)^2$, which is comparable with the formula obtained by Noyes and Whitney for the solution of benzoic acid or lead chloride in water (compare A., 1897, ii, 479). W. G.

Certain Conditions of Oxidation of Organic Compounds by Permanganate. A. G. DOROSCHEVSKI and G. S. PAVLOV (*J. Russ. Phys. Chem. Soc*, 1915, **47**, 1313—1326. Compare A., 1915, ii, 331).—Investigations have now been made on the coupled oxidation of further organic compounds by permanganate and ferrous oxide or other inductor.

Both mannitol and glycerol are readily oxidised by permanganate in presence of a ferrous salt, increase of the proportion of the latter being accompanied by diminution of the induction factor; ferric salts appear to be without influence on the oxidation. Similar results are obtained with dextrose, lævulose, and sucrose. The induction factor in the case of lævulose is greater than with dextrose, and the ratio increases with increase in the quantities of the two sugars. Thus, lævulose is more readily oxidised than dextrose, and a solution of the mixed sugars, having virtually no optical rotation ($+0·04°$) was found to be decidedly dextrorotatory ($+0·26°$) after the oxidation had proceeded for some time, in spite of the dilution which takes place. Preliminary hydrolysis facilitates the oxidation of sucrose, this fact being probably of importance in the animal organism, in which such hydrolysis always occurs; the oxidation of invert-sugar represents the summation of the oxidations of dextrose and lævulose.

Thus not only the higher alcohols, but also keto- and aldehydo-alcohols, are capable of oxidation by permanganate in conjunction with a ferrous salt; in general, however, the introduction into the alcohol molecule of a new chemical function lowers its capacity for coupled oxidation, and conversion of an alcohol into the corresponding acid may result in complete loss of such capacity.

The action of oxalic acid or stannous chloride as inductor was also investigated in certain cases of oxidation by means of permanganate. The presence of stannous chloride induces the oxidation of mannitol, glycerol, formic acid, etc., and also to some extent that of acetic and succinic acids, which are not oxidised in presence

of ferrous sulphate. It is possible that with each organic compound there exists a most active inductor for any given actor.

As regards the influence of manganous sulphate, it is known that in other cases this salt acts sometimes as a positive and sometimes as a negative catalyst. The latter function is clearly revealed in the oxidation of alcohols by permanganate and ferrous sulphate, this being either retarded or completely inhibited by the protecting action of manganous sulphate. This action appears to have a bearing on the character of the curves expressing the connexion between the induction factor (as ordinates) and the quantity of acceptor in the instances mentioned above. The fact that these curves tend to become parallel to the axis of abscissæ may, indeed, depend largely on the fact that a continually diminishing amount of permanganate is used to oxidise the acceptor owing to the protecting influence of the manganous sulphate which accumulates in the solution as the ferrous sulphate is oxidised. Further, when stannous chloride is employed as inductor, stannic chloride is found to exert a protecting action. Thus, in so far as the reactions investigated by the authors are concerned, the secondary products exert a protecting action, the result being somewhat similar to the principle which states that change in the constitution of a system is accompanied by processes resisting further change.

The protecting action of manganous salts may explain the fact that alcohols, sugars, formic acid, and many other compounds are easily and completely oxidised by permanganate in an alkaline medium, but do not undergo oxidation in an acid medium, no manganous compounds being formed in solution in the former case.

T. H. P.

A Laboratory Circulating Pump. John Stanley Morgan (T., 1915, **107**, 1710—1711).—An improvised form of circulating pump is described in which, by making use of the air-lift, an ordinary water-pump is made to furnish the required motive power; it can be used for the supply of water from a thermostat to the jackets of polarimeters, barometers, or other forms of apparatus. H. M. D.

A Safe Automatic Gas Seal for the Preservation of Reduced Solutions. Paul Verbeek (*Chem. Zeit.*, 1915, **39**, 840—841).—Carbon dioxide is generated in a small conical flask by the action on marble of dilute acid, which enters through a dropping funnel with a capillary stem. This flask is connected with two others containing water which are in communication by means of a glass tube extending to the bottom of both flasks. Alterations of pressure will cause the water to pass over into one or other of the flasks, but the water seal will not thereby be broken. The third flask is joined through a distilling trap with the flask containing the reduced solution, and exit is given to the atmosphere from the latter through a screw clip. The apparatus is operated by opening this clip and the tap of the dropping funnel so that acid enters the flask containing the marble, and carbon dioxide passes through all the flasks and displaces the air. The screw clip is then closed,

and the tap of the dropping-funnel being left open, the apparatus is left to itself. Alterations of pressure in the flask containing the reduced solution automatically equalise themselves either by expelling gas from the flask or by drawing more carbon dioxide in as required. Other gases may be used instead of carbon dioxide; thus, for example, hydrogen by replacing the marble with zinc and the water seal in the central pair of flasks by a permanganate solution. The apparatus can also be employed for avoiding the danger of sucking back in saturating a liquid with a gas. G. F. M.

An Apparatus for Evaporating Aqueous Extracts by Means of a Current of Air. T. B. ALDRICH (*J. Biol. Chem.*, 1915, **23**, 255—259).—The main feature of the apparatus consists in the employment of two pipes in the shape of an inverted **U**, one being enclosed within the other. The outer one terminates in the hood of a draught chamber, whereas the inner one is prolonged into the chamber itself, and terminates in two oblong movable orifices which can be adjusted so as to deliver a current of air over the surfaces of the liquid to be evaporated. This air current is supplied by a blower placed at the other end of the inner tube, and is heated by a gas burner placed in the end of the outer tube which is distal from its termination in the draught cupboard. By this arrangement the products of combustion of the burner can be kept separate from the warmed air used in the evaporation. The apparatus is figured in the text. S. B. S.

An Extraction Apparatus. A. A. BESSON (*Chem. Zeit.*, 1915, **39**, 860).—An extraction apparatus of simple construction is described, consisting of a flask having a long, wide neck with a constriction at the bottom on which rests an extraction thimble, leaving only a small annular space between it and the neck of the flask. The condenser, which is of the Storch type with internal cooling, fits closely into the neck just above the thimble. The whole apparatus is only 15—16 cm. high and can conveniently be weighed on an analytical balance. G. F. M.

Apparatus for the Production of Gases. L. BERTIAUX (*Ann. Chim. anal.*, 1915, **20**, 239—240).—In the gas generator described the substance from which the gas is to be evolved is contained in a vessel provided with a delivery tube and a draw-off tap, and the acid or other solution is admitted through a tapped tube from an upper reservoir. A tube connects the upper parts of the lower vessel and the reservoir, and the upper part of the latter is in turn connected with a manometer which shows the pressure in the apparatus and also acts as a safety-valve. Various forms of the apparatus are illustrated. W. P. S.

Inorganic Chemistry.

Chlorous Acid and Chlorites. G. BRUNI and G. LEVI (*Gazzetta*, 1915, **45**, ii, 161—179).—The authors have prepared various chlorites and investigated certain of their physical properties. The analogy between chlorites and nitrites is shown by the methods of preparation and by the existence of the *compounds*, $AgClO_2,NH_3$, $AgClO_2,2NH_3$, and $AgClO_2,3NH_3$, which are similar to those formed from silver nitrite and ammonia.

Barium chlorite may be obtained absolutely free from chloride by the action of a mixture of chlorine dioxide and carbon dioxide, free from chlorine, on barium peroxide suspended in hydrogen peroxide solution. The sodium salt may be obtained from barium chlorite and sodium sulphate, the liquid being evaporated in a vacuum at the ordinary temperature; the ammonium and hydroxylamine salts are not obtainable in this way. The basic *mercuric chlorite*, $3Hg(ClO_2)_2,HgO$ (?), obtained from barium or potassium chlorite and mercuric nitrate, forms a bright red, crystalline precipitate, and explodes when dried; the yellow, mercurous salt reddens in the air, and decomposes spontaneously on drying.

A number of the known reactions for soluble chlorites have been confirmed, and the following new ones added. No precipitate with mercuric chloride; red precipitate with mercuric nitrate in neutral and not too dilute solution; with mercurous nitrate, a yellow precipitate, becoming white with excess of the reagent; with neutral ferrous sulphate solution, a brownish-yellow coloration, and, in the hot, an ochre-yellow deposit and liberation of chlorous vapours; oxidation of potassium ferrocyanide to ferricyanide in acid solution; brucine and diphenylamine show the same behaviour with chlorites as with chlorates; with reagents for nitrous acid, chlorites slowly give colorations analogous to those given by nitrites, probably owing to the oxidising action exerted. With concentrated sulphuric acid, solid chlorites deflagrate more energetically than the chlorates.

Electrical conductivity measurements of potassium, silver, and barium chlorites give for the mobility of the ion ClO_2' at 25° the values 50·6—51·7, the mean being 51·0, which is less than that for the ion ClO_3' and less still than that for ClO_4'. Similar measurements with sodium, potassium, and silver nitrites give the mean value 75·4 for the mobility of the ion NO_2' at 25°, this being greater than that for the ion NO_3'. Cryoscopic investigation of potassium chlorite in aqueous solutions gives the respective values 0·930, 0·920, 0·935, and 0·959, for α with solutions containing 1·0656 grams of the salt in 10, 15, 20, or 40 grams of water.

The decomposition of barium chlorite was studied in the bomb calorimeter, and found to take place according to the equation $Ba(ClO_2)_2 = BaCl_2 + 2O_2 + 48{\cdot}6$ Cal. From this follows the equations $Ba + Cl_2 + 2O_2 = Ba(ClO_2)_2(\text{solid}) + 148{\cdot}4$ Cal., and $BaCl_2 +$

$2O_2 = Ba(ClO_2)_2 - 48{\cdot}6$ Cal., $Ba(ClO_2)_2 + O_2 = Ba(ClO_3)_2 + 22{\cdot}8$ Cal., and $Ba(ClO_3)_2 + O_2 = Ba(ClO_4)_2 + 30{\cdot}2$ Cal. Consequently, in compounds containing chlorine in different degrees of oxidation, the formation is the less endothermic or the more exothermic the higher the degree of oxidation. This apparently paradoxical introduction of successive atoms of oxygen with continually increasing energy is in agreement with Angeli's observations on oxygenated nitrogen compounds (*Rend. Accad. Lincei*, 1894, [v], **3**, i, 510).

T. H. P.

Rhythmic Crystallisation of Sulphur. FRITZ KÖHLER (*Kolloid Zeitsch.*, 1915, **17**, 10—11).—Micro-structures of rhythmic character are formed when thin layers of liquid sulphur are allowed to crystallise. These are illustrated by photographs. The author does not agree with the explanation given for the formation of these structures by von Fischer-Treuenfeld (A., 1915, ii, 553). In his opinion the rhythmic character of the crystallisation process is due to the rate of crystallisation exceeding the rate of diffusion. This is consistent with the fact that the phenomenon is readily shown in the crystallisation of viscous liquids. H. M. D.

Internal Temperature of Sulphur Furnaces. STEFANO PAGLIANI (*Ann. Chim. Applicata*, 1915, **4**, 268—270).—Reply to criticism, appearing in *L'Industria* (1915, No. 42, Milan), on the author's work (A., 1915, ii, 766). T. H. P.

Preparation of Thionyl Chloride and Sulphur Tetrachloride. CHEMISCHE FABRIK BUCKAU (D.R.-P. 284935; from *J. Soc. Chem. Ind.*, 1915, **34**, 1092).—Carbonyl chloride reacts with sulphur dioxide at temperatures above 200° with the formation of thionyl chloride and sulphur tetrachloride according to the equations: $SO_2 + COCl_2 = SOCl_2 + CO_2$ and $SO_2 + 2COCl_2 = SCl_4 + 2CO_2$. The first reaction predominates at lower temperatures and with excess of sulphur dioxide, and by suitable adjustment of conditions one or other of the reactions may be almost entirely excluded. The reactions are carried out by passing the gases over a heated contact substance, such as wood charcoal, and the carbonyl chloride may be partly or entirely replaced by a mixture of carbon monoxide and chlorine, or carbon monoxide and sulphuryl chloride may be employed. G. F. M.

Action of Thionyl Chloride on Sulphides. H. B. NORTH and C. B. CONOVER (*J. Amer. Chem. Soc.*, 1915, **37**, 2486—2490).—The action of thionyl chloride on the sulphides of zinc, cadmium, silver, arsenic, antimony, iron, copper, tin (stannic), and mercury has been studied. It is shown that a reaction occurs when the two substances are heated in a sealed tube at 150—200° for several days. In general, the reaction may be represented by the equation $MS + 2SOCl_2 = MCl_2 + SO_2 + S_2Cl_2$. The case of ferrous sulphide presents a slight difference, for here an oxidation occurs, and ferric chloride is formed according to the equation $6FeS + 16SOCl_2 = 6FeCl_3 + 8SO_2 + 7S_2Cl_2$. J. F. S.

Vapour-pressure Investigations of the Fusion Products of Iodine with Sulphur, Selenium and Tellurium. ROBERT WRIGHT (T., 1915, **107**, 1527—1531).—A simple method is described for the measurement of the pressure of the iodine vapour in equilibrium with the solid products which result from the fusion of iodine with sulphur, selenium, and tellurium. Products which contain a large excess of iodine have in all three cases the same vapour pressure as pure iodine at the same temperature. With excess of sulphur and selenium, the same result was obtained, but with excess of tellurium, the iodine vapour pressure is very small up to 150°. The results show that in no case are solid solutions formed, that sulphur and selenium do not combine with iodine on fusion, but that tellurium forms a compound, TeI_4. H. M. D.

Metallographic Study of the System Tellurium–Selenium. YASUKIYO KIMATA (*Mem. Coll. Sci. Kyoto*, 1915, **1**, 119—121).—Tellurium and selenium form two series of solid solutions. These meet at 95% Se and 130°, at which temperature the liquid and solid phases have the same composition. The two branches of the liquidus and solidus curves intersect at a sharp angle, suggesting a eutectic, but all the alloys are microscopically homogeneous. Whether a compound is formed at this point is undetermined.

C. H. D.

The Imide Character of Hydronitric Acid (Azoimide). I. Synthesis of Azidodithiocarbonic Acid. FRITZ SOMMER (*Ber.*, 1915, **48**, 1833—1841).—In accordance with its usual formulation as an imino-compound, azoimide behaves in the same manner as a secondary amine towards carbon disulphide; analogous to the formation of the compound $NEt_2{\cdot}CS{\cdot}SH,NHEt_2$ from diethylamine and carbon disulphide, sodium azoimide and carbon disulphide react with formation of the sodium salt of azidodithiocarbonic acid, $N_3{\cdot}CS{\cdot}SNa$.

Sodium azidodithiocarbonate, $N_3{\cdot}CS_2Na,4H_2O$, is obtained by the interaction of carbon disulphide and an aqueous solution of sodium azoimide at 40—50°, a pale yellow solution being obtained, which yields colourless prisms on evaporation; the salt is fairly permanent if kept below 10° in a closed vessel. It explodes when heated, being more explosive in the anhydrous condition.

The corresponding *potassium* salt, obtained in a similar manner, is a crystalline solid which explodes violently when pressed. The *barium* salt was also prepared, forming hexagonal tablets, $(N_3CS_2)_2Ba,5H_2O$, which were comparable with the sodium salt in explosive nature, the anhydrous salt being somewhat more explosive.

Salts of certain of the heavy metals were prepared by precipitation from solutions of the sodium salt. The fact that the colour of the products in some cases deviated from the usual colour of the salts of the metal and their occasional solubility in organic solvents, indicate that in common with the xanthic acids, azidodithiocarbonic acid tends to form complex salts of abnormal dissocia-

tion. Most of these salts of the heavy metals were exceedingly explosive. *Silver* salt, amorphous; *cupric* salt, yellow; *mercuric* salt, colourless crystals, soluble in ether, carbon disulphide, and ethyl acetate; *mercurous* salt, colourless; *lead* salt, yellowish-white; *thallium* salt, yellowish-white; *cadmium* salt, colourless needles; *bismuth* salt, yellow; *zinc* salt, colourless.

The addition of ferric chloride to the solution of the sodium salt, instead of effecting the precipitation of the ferric salt of the acid, caused oxidation to the *disulphide*, $S_2(CS{\cdot}N_3)_2$, which separated in needles; a similar result was obtained with other oxidising agents. This compound is so explosive that even on warming in aqueous suspension a violent explosion may ensue.

By treating the concentrated solution of sodium azidodithiocarbonate with hydrochloric acid it is possible to obtain free *azidodithiocarbonic acid*; this by oxidation can be converted into the corresponding disulphide. Details of these compounds will be published later. D. F. T.

Explosive Mixture of Phosphorus and Liquid Air. ARNALDO PIUTTI (*Atti. R. Accad. Lincei*, 1915, [v], **24**, ii, 252—253).—Yellow phosphorus does not combine with liquid oxygen, but, after removal from the liquid, explodes with extreme violence if struck, touched with hot iron, or subjected to the action of an electric spark. This property is conferred on the phosphorus only by actual contact with the liquid oxygen. With highly compressed red phosphorus or with ordinary sulphur, no explosion occurs under the above conditions, but the substance burns vigorously. T. H. P.

Fibrox. E. WEINTRAUB (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 267—284).—When silicon is heated in a graphite crucible at 1400—1500° in a gas furnace, a small quantity of calcium fluoride being present, the crucible becomes filled in a few hours with a fibrous mass of silicon oxycarbide. After breaking away the slag and re-heating, a further quantity may be obtained. This material, known as fibrox, is made up of very fine, amorphous threads, sometimes carrying minute beads of vitreous silica. It is formed by reactions in the state of vapour, and experiments in an electric furnace show that the presence of carbon dioxide is necessary. The density varies from 1·84 to 2·2, increasing with the percentage of silicon. The apparent density of the fibrous mass is only 0·0025—0·0030, or 2·5—3·0 grams per litre. The thermal resistance in the loosely packed condition is very high, but diminishes with rising temperature. C. H. D.

The Temperature of Reaction between Acheson Graphite and Magnesia. O. L. KOWALKE and D. S. GRENFELL (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 221—239. Compare Slade, T., 1908, **93**, 327; Lebeau, A., 1907, ii, 460).—When electrically fused magnesium oxide is powdered and heated in a granular carbon resistance furnace in contact with graphite, the temperature being measured by an optical pyrometer sighted on a hollow graphite

"black-body," the reaction $MgO+C=Mg+CO$ begins slowly at 1950°, and becomes very violent at 2030°. This temperature is sufficiently constant to serve as a fixed point for the calibration of optical pyrometers. When a vacuum furnace is used observations are difficult on account of the fumes produced in the reaction.
C. H. D.

Graphitic Acid. L. BALBIANO (*Ann. Chim. Applicata*, 1915, **4**, 231—245).—Investigation of preparations of graphitic acid and graphitic oxide obtained from three different samples of graphite shows that the compositions of these products vary with the method of preparation and with the quality of the graphite employed. Brodie's method (*Phil. Trans.*, 1859, **149**, 249) gives a graphitic acid which contains C=57·35, H=1·47, and O=41·17, these figures corresponding with the formula $C_{13}H_4O_7$; for the product obtained by Staudenmaier's method (A., 1898, ii, 472; 1899, ii, 481) the composition is C=59·2, H=1·4, and O=39·4, and the formula $C_{14}H_4O_7$. With graphitic oxide the analytical numbers also correspond with the formula $C_{13}H_4O_7$ or $C_{14}H_4O_7$. These graphitic products, which deflagrate when rapidly heated and vary in colour with the nature of the original graphite and the method of preparation, are found, however, to be merely adsorption products of graphite, water, carbon monoxide, and dioxide varying in composition between narrow limits. They have no acidic or quinonic functions, and it is suggested that they be termed yellow, green, or black *hydrocarboxygraphites*, instead of graphitic acid and oxide. T. H. P.

The System: Sodium Sulphate–Sodium Chromate–Water. ISAKICHI TAKEUCHI (*Mem. Coll. Sci. Kyoto*, 1915, **1**, 249—255).—The equilibrium of this system has been determined at 15° and 25°. The decahydrates of sodium sulphate and chromate are miscible in all proportions at 15°. At 25° the solubility curve consists of three branches, corresponding with decahydrate solid solution from 0 to 34 mol. % of chromate, anhydrous sulphate, and sodium chromate hexahydrate respectively. The limit of miscibility of the decahydrate crystals coincides approximately with

$$2Na_2SO_4,Na_2CrO_4,30H_2O,$$

but the existence of a double salt has not been definitely proved.
C. H. D.

Allotropy of the Ammonium Haloids. I. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 446—458).—According to Wallace (A., 1910, ii, 208), ammonium chloride and ammonium bromide are enantiotropic, having transition temperatures at 159° and 109° respectively. Further experiments with ammonium chloride have shown that the cooling-curve method, which was used in the determinations referred to, gives a much lower temperature than the true transition temperature in consequence of the retarded transformation. In presence of glycerol or mannitol, which act as catalysts, the thermal method yields much better results in that the temperatures indicated by cooling and

heating curves are in fairly close agreement. The value thus obtained for the transition temperature is 184·5°. The same result has been arrived at on the basis of measurements of the solubility of ammonium chloride in water between 160° and 205°. If x represents the number of mols. of salt in one mol. of saturated solution, then it is found on plotting $\log x$ against $1/T$ that two straight lines are obtained which intersect at 184·5°. The equation for the solubility of the modification which is stable at the lower temperatures is $-\log x = 464{\cdot}5/T - 0{\cdot}5400$, and for that stable at higher temperatures $-\log x = 327{\cdot}8/T - 0{\cdot}2412$.

In a discussion of the nomenclature of isomerism the author considers that allotropy may be conveniently used to include all cases of isomerism and polymorphism. Where two or more solid modifications occur, the allotropy would be distinguished as phase allotropy to distinguish it from molecular allotropy. H. M. D.

Solubility of Calcite in Water in Contact with the Atmosphere and its Variation with Temperature. ROGER C. WELLS (*J. Washington Acad. Sci.*, 1915, **5**, 617—622).—The solubility of calcite in water exposed to the air has been determined at a series of temperatures. The method consisted in placing powdered calcite in water in Jena flasks and bubbling air, of average content 3·18 parts of carbon dioxide per 10,000, through it until saturation occurred. The content of calcium carbonate was then estimated by titration with 0·02N-sodium hydrogen sulphate. Saturation required usually about eighty days. The following results expressed in parts of calcium carbonate per million were obtained: at 1°, 82; 21°, 60; 22°, 57; 23°, 57; 30°, 55. The rate at which saturated solutions deposit calcite on keeping was also determined. The results of the decreased solubility with increase in temperature are discussed from a geo-chemical point of view in connexion with the deposits of the Mississippi and the presence of marble in certain coral islands in the Philippines. J. F. S.

The Reactions between Several of the Salts contained in [Natural] Waters at the Boiling Point. P. PETIT (*Mon. Sci.*, 1914, [v], **4**, 537—541).—Whilst the precipitation of calcium carbonate from dilute solutions of the hydrogen carbonate is but little influenced by external conditions, the similar precipitation of magnesium is greatly dependent on the method of heating, and the size of the vessel and the condition of its walls. After one hour's boiling the quantity of calcium carbonate remaining in solution is about 17 mg. per litre, and is independent of the initial concentration. With magnesium carbonate, on the other hand, the percentage precipitated decreases with decrease in initial concentration, and for concentrations of about 110 mg. per litre 50% at most is eliminated by an hour's boiling in clean vessels. Water containing both calcium and magnesium hydrogen carbonates loses nearly all its calcareous matter when the calcium considerably predominates; the magnesium is precipitated as if it were alone. Sodium chloride diminishes the precipitation of calcium carbonate,

and also of magnesium carbonate, except in minute quantities, in which case the precipitation of magnesium carbonate is increased by about 10%. From a water containing calcium hydrogen carbonate and magnesium sulphate with a preponderance of calcium the precipitation of calcium carbonate is almost unaffected by the presence of the magnesium salt, but with a preponderance of magnesium precipitation of calcium carbonate is diminished, and in neither case is much magnesium carbonate eliminated. Calcium sulphate in excess facilitates the precipitation of magnesium carbonate, and, with a preponderance of 21 : 1, 92% of the latter is eliminated. With increasing excess of magnesium hydrogen carbonate, increasing quantities of calcium carbonate are precipitated from a sulphate solution. G. F. M.

Formation of Magnesium Suboxide in the Electrolytic Preparation of Magnesium. FRANCIS C. FRARY and HARRY C. BERMAN (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 209—219).—When magnesium and potassium chlorides are electrolysed in a graphite crucible, small masses of a dark substance which evolves hydrogen with water are found in the mass after cooling. The gas so obtained contains 95% of hydrogen, the remainder being nitrogen. The dark solid oxidises so rapidly that it has not been found possible to make an analysis. It is without action on a solution of anhydrous nickel chloride in absolute alcohol, whilst metallic magnesium powder rapidly precipitates nickel. The dark substance is not formed when oxygen is completely excluded from the electrolyte by melting in a stream of hydrogen chloride, and continuing the passage of the gas during electrolysis. Adding a little magnesium oxide to this electrolyte results in the formation of suboxide. C. H. D.

Atomic Weight of Cadmium. W. ŒCHSNER DE CONINCK and GÉRARD (*Compt. rend.*, 1915, **161**. 676—677).—The substance used was cadmium carbonate, which was prepared by dissolving metallic cadmium in sulphuric acid, and passing a current of hydrogen sulphide for several hours; the precipitate after washing was dissolved in concentrated hydrochloric acid, the excess of acid evaporated off, and a large excess of a concentrated solution of ammonium carbonate added, cadmium carbonate alone being precipitated. This process was repeated three times. A definite weight of the dried cadmium carbonate was ignited in a special crucible in a current of pure hydrogen, and from the ratio $CdCO_3$: Cd the atomic weight of cadmium was calculated. The mean of five determinations was 112·32. W. G.

Red Lead. JAROSLAV MILBAUER (*Chem. Zeit.*, 1915, **39**, 858—859).—The presence of silver in lead oxide has a favourable effect on the formation of red lead at low temperatures; at 300° 27% of Pb_3O_4 was obtained, against 9% in the absence of silver. At higher temperatures no effect was observed on the formation of red lead. Bismuth is also indifferent, but zinc and antimony cause an appre-

ciable reduction in the amount of the higher oxide formed. Iron and copper likewise have no accelerating effect, and they tend to influence the colour unfavourably. The formation of red lead is accelerated by using amorphous preparations of lead oxide, and by employing air or oxygen under pressure (Austrian Pat. 58167). The equilibrium conditions remain thereby unaltered. The preparation of pure red lead by fusion of lead oxide with potassium nitrate (A., 1914, ii, 464) is not possible owing to the reversibility of the reaction. A new wet method for the preparation is suggested, namely, by boiling lead peroxide (3 mols.) and lead oxide (2 mols.) with concentrated aqueous potassium hydroxide. The product is 100% pure, and its colour varies from purplish-red to bright red with increasing concentration of the alkali. G. F. M.

Alloys of Tellurium with Lead. MASAO KIMURA (*Mem. Coll. Sci. Kyoto*, 1915, **8**, 149—152. Compare Fay and Gillson, A., 1902, ii, 260).—This system is of a simple type, the only compound melting at 904°, with one eutectic point at 412° and 24% Pb, the other eutectic practically coinciding with pure lead. Solid solutions are not formed to any appreciable extent. The micro-structure is simple, and accords with the thermal diagram. C. H. D.

Metallography of the System Thallium-Selenium. TAKEJIRO MURAKAMI (*Mem. Coll. Sci. Kyoto*, 1915, **1**, 153—159).—The equilibrium diagram of this system is complex. There are three compounds, of which two present themselves as maxima on the freezing-point curve, whilst the third decomposes below its melting point. There are three eutectic points, at 281°, 283°, and 150° respectively. These correspond with alloys containing 1%, 21%, and 52% of selenium respectively.

Tl_2Se melts at 368°, and TlSe at 310°. Tl_2Se_3 decomposes at 265°, and undergoes a transformation at 165°. There are two gaps of miscibility in the liquid state, extending from 4 to 14·5% Se, and from 55 to 97·5% Se. All the compounds are brittle, and the micro-structure is in accordance with the thermal diagram. C. H. D.

The Structure of Electrolytic Copper. M. VON SCHWARZ (*Intern. Zeitsch. Metallographie*, 1915, **7**, 124—173. Compare Faust, A., 1912, ii, 1173).—Very large crystals, 5 cm. or more in length, may be obtained from an ordinary sulphate bath for the electrolytic deposition of copper, the temperature being 1—7°, and all agitation being avoided. The crystals are repeatedly twinned octahedra, and their orientation is confirmed by etching. The growth of crystal grains in massive electrolytic copper on annealing is also described. The larger grains absorb the smaller, except where the metal has been locally strained. The very small grains produced by straining grow much more rapidly than the others at first, but this difference only persists for a short time of annealing.

Electrolytically deposited crystals grow parallel to the surface

of the cathode, one octahedral face being in contact with the cathode, and elongation taking place along a trigonal axis. Twinning occurs when these crystals are annealed, but again disappears after prolonged annealing.

The effect of pressure on isolated crystals in causing the formation of new crystal centres is also shown by the experiments, and the observations are utilised for a discussion of the hypothesis of an amorphous modification produced by flow, and also present at the crystal boundaries in cast metals. C. H. D.

Micro-structural Changes accompanying the Annealing of Bronze. HENRY S. RAWDON (*J. Washington Acad. Sci.*, 1915, **5**, 589—591).—Specimens of bronze containing 88% of copper, 10% of tin, and 2% of zinc have been annealed at various temperatures. The cast alloys lose their dendritic structure at 800°, but without any change in the form of the crystal grains. Bronze which has been deformed in the cold recrystallises completely, the depth of the layer affected by the deformation remaining constant as the crystals increase in size. C. H. D.

Cerium Alloys. I. The Constitution of Cerium–Copper Alloys. FRANZ HANAMAN (*Intern. Zeitsch. Metallographie*, 1915, **7**, 174—212).—The metallic cerium used contains cerium 96·71%, iron 0·50%, the remainder being cerite metals. It melts at 715°, and as a small quantity of an iron eutectic is undoubtedly present the true melting point of cerium must be close to 720°. The metals are melted in unglazed porcelain crucibles, under a layer of sodium chloride or mixed potassium and sodium chlorides. The cerium is best added to molten copper, except for alloys containing more than 80% Ce, for which the reverse process is used. The thermo-couple is protected by a very thin tube of unglazed porcelain, and the cooling curves are determined by the inverse-rate method.

The freezing-point curve has two well-marked maxima, corresponding with a compound Cu_6Ce, which melts at 935°, and Cu_2Ce, melting at 820°. There are also two compounds which are formed by reactions between solid and liquid, thus giving rise to breaks in the freezing-point curve; Cu_4Ce at 780°, and CuCe at 514°. There are three eutectic points, at 875°, 757°, and 415°, occurring at 17%, 44%, and 84% of cerium respectively. Solid solutions are not formed. The alloys richest in cerium contain traces of a ternary eutectic of copper, cerium, and iron.

The hardness curve of the alloys, determined by Brinell's method, has two pronounced maxima, corresponding with the compounds Cu_6Ce and Cu_2Ce, the former being nearly four times as hard as copper.

The micro-structure of the alloys is described in detail and illustrated. The colour of the alloys resembles that of copper as far as the first eutectic; from that point to the third eutectic it resembles that of bronze, and then becomes steel-grey. Only those which lie between 55% and 85% Ce are pyrophoric. Those containing less than 30% Ce are stable and retain their colour in air; richer alloys soon disintegrate. C. H. D.

Calorising Metals. W. E. RUDER (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 253—266).—The process of "calorising" consists in heating the metal at 700—950° in a mixture of powdered aluminium and alumina, with the addition of about 1% of ammonium chloride. Copper and brass are heated at 700—800°, iron and steel at 900—950°, a larger proportion of metallic aluminium in the mixture being required by the latter metals. The time is usually two to three hours.

Aluminium alloys superficially with the metal, and gradually diffuses inwards. When heated for a long time at or above 1000° the greater part of the layer of alloy disappears owing to diffusion, and a thin layer of oxide remains on the surface. Nickel wire or ribbon may be coated with a layer sufficiently thick to resist oxidation without injuring its flexibility.

The stages in the diffusion are illustrated by photo-micrographs.

C. H. D.

Manganese-Bismuth Alloys. E. BEKIER (*Intern. Zeitsch. Metallographie*, 1914, **7**, 83—92. Compare Parravano and Perret, A., 1915, ii, 565).—Powdered manganese may be dissolved in molten bismuth by heating very cautiously in unglazed porcelain tubes, around which a reducing atmosphere is maintained. There is a eutectic point very close to pure bismuth. Only a single compound is formed, the composition of which lies between MnBi and Mn_2Bi. Partial miscibility in the liquid state extends from 39% to practically 100% of manganese, the horizontal part of the curve being at 1240°. C. H. D.

The Iron-Carbon Equilibrium Diagram. OTTO RUFF (*Ferrum*, 1915, **12**, 121—123. Compare A., 1913, ii, 56).—The cementite which is decomposed, with formation of graphite, during the cooling of liquid iron-carbon alloys is that which is in excess of the equilibrium concentration, but below the saturation concentration. Any excess above this latter concentration separates as free cementite. The true eutectic temperature is 1125°, or possibly nearly 1130°; the pseudo-eutectic temperature is higher, about 1138°. C. H. D.

The Pseudo-eutectic Temperature of the Iron-Carbon Alloys. OTTO RUFF and WALTER BORMANN (*Ferrum*, 1915, **12**, 124—126. Compare preceding abstract).—The true eutectic temperature is that at which the iron solid solution and cementite solidify in the same ratio as that in which they are present in the liquid. The pseudo-eutectic temperature is that at which the liquid is simultaneously saturated for cementite and graphite. Experiments to determine the latter temperature must be made with hypereutectic alloys; otherwise the absence of graphite nuclei causes great undercooling.

An iron containing carbon 4·13, silicon 0·074, sulphur 0·006, manganese 0·15, phosphorus 0·02, and copper 0·005% is melted in a graphite crucible, the atmosphere of the electric carbon furnace

containing about 30% of carbon monoxide. The pseudo-eutectic temperature is found quite sharply, 1138·8°±1°. It is slightly raised by addition of silicon, and lowered by that of manganese.

C. H. D.

Can the Dissociation Theory be Applied to Solid Solutions in Steels? EDWARD D. CAMPBELL (*J. Amer. Chem. Soc.*, 1915, **37**, 2522).—Owing to an ammeter used in the experiments described previously reading too high (A., 1915, ii, 779) a correction of from 0·42 to 0·48 microhms is to be applied to the figures there given. This correction does not effect the significance of the figures or the deductions drawn from them.

J. F. S.

The Behaviour of Slag Enclosures in Acid Steel. F. GIOLITTI and S. ZUBLENA (*Intern. Zeitsch. Metallographie*, 1914, **7**, 35—82. Compare Giolitti and Tavanti, A., 1915, ii, 57).—Specimens are cut from the sound central portion of an ingot of acid open-hearth steel containing carbon 0·38%, manganese 0·60%, silicon 0·22%, sulphur 0·008%, phosphorus 0·02%, and nickel 2·02%. In all cases the enclosures of grey sulphide slag are found in the central part of the ferrite masses, completely separated from the pearlite. When heated for four hours at a constant temperature of 1060° in carbon dioxide, slight decarburisation takes place, and the slag enclosures are now frequently in contact with pearlite. The effect is more marked at 1100°. In carbon monoxide at 1100° the carburised portion shows the ferrite and slag completely independent. This occurs whenever carburisation takes place, whilst ferrite formed during an oxidising process encloses the slag. The results are attributed to the influence of the slag on the oxidation of the carbide and consequent liberation of ferrite.

Repeating the experiments with a steel containing carbon 0·40%, manganese 0·58%, silicon 0·20%, sulphur 0·006%, phosphorus 0·03%, and nickel 1·98%, also of acid open-hearth origin, the same changes are found to take place still more readily.

The only slag enclosures which exert an influence on the distribution of ferrite are those of light grey colour, usually regarded as manganese sulphide.

C. H. D.

Corrosion of Molybdenum Salts. LESLIE AITCHISON (T., 1915, **107**, 1531—1538).—The influence of molybdenum on the corrodibility of "high-speed" steels has been investigated by comparative experiments with a standard pure carbon steel and a series of steels containing approximately the same percentage of carbon and quantities of molybdenum varying from 2·5 to 20%. The results obtained with 3% sodium chloride and 1 to 10% sulphuric acid solutions show that the addition of small quantities of molybdenum is accompanied by a considerable increase in the corrodibility of the steel. In the salt solution the corrosion increases somewhat with further increase in the molybdenum content, but in the acid solutions this is accompanied by a diminution in the corrodibility. In tap-water, molybdenum first produces a slight diminution and then a slight increase.

The results obtained in the investigation of the action of 10% sulphuric acid on the steels shows that no trace of molybdenum dissolves until the proportion of molybdenum exceeds that required for the formation of carbide (19—20%). This is in agreement with the micro-structure of the samples. H. M. D.

An Acid-resisting Alloy to Replace Platinum in the Construction of a Bomb Calorimeter. S. W. PARR (*J. Amer. Chem. Soc.*, 1915, **37**, 2515—2522).—After a large number of experiments an alloy has been obtained which on account of its high tensile strength, resistance to acids, and closely-grained structure has been used for making calorimetric bombs. This alloy, which melts at 1600°, renders the use of a platinum lining quite unnecessary. It has the following composition; 6·42% Cu, 0·98% Mn, 1·04% Si, 2·13% W, 60·65% Ni, 1·09% Al, 0·76% Fe, 21·07% Cr, and 4·67% Mo. J. F. S.

The Monoclinic Double Sulphates containing Ammonium. Completion of the Double Sulphate Séries. A. E. H. TUTTON (*Phil. Trans.*, 1915, *A.*, 216, 1—62).—The crystallographic and optical properties of the double sulphates of the series $R_2M(SO_4)_2,6H_2O$, in which R is ammonium and M represents magnesium, zinc, and iron, have been described in previous papers (compare T., 1905, **87**, 1123; A., 1913, ii, 603). The present paper gives an account of the properties of the five remaining double salts in which M represents nickel, cobalt, manganese, copper, and cadmium. The densities of the corresponding potassium, rubidium, and cæsium double sulphates have been redetermined by the immersion method, the values previously obtained by the pyknometer method being rather low. The chief experimental data of interest to the chemist are given in the following summary:

Ammonium nickel sulphate—monoclinic,

$$[a:b:c=0·7373:1:0·5000 \quad \beta=106°57'];$$

D_4^{20} 1·923. For corresponding potassium salt D_4^{20} =2·237, rubidium 2·586, cæsium 2·872.

Ammonium cobalt sulphate—monoclinic,

$$[a:b:c=0·7386:1:0·4975; \beta=107°2'];$$

D_4^{20} 1·901. Potassium salt D_4^{20}=2·219, rubidium 2·567, cæsium 2·844.

Ammonium manganese sulphate—monoclinic,

$$[a:b:c=0·7400:1:0·4931; \beta=106°51'];$$

D_4^{20} 1·831. Rubidium salt D_4^{20} =2·461, cæsium 2·740.

Ammonium copper sulphate—monoclinic,

$$[a:b:c=0·7463:1:5066; \beta=106°9'];$$

D_4^{20} 1·926. Potassium salt D_4^{20} =2·233, rubidium 2·574, cæsium 2·858.

Ammonium cadmium sulphate—monoclinic,

$$[a:b:c=0·7364:1:0·4931; \beta=106°41'];$$

D_4^{20} 2·061. Rubidium salt D_4^{20} 2·695, cæsium salt 2·957.

The results obtained for the above five ammonium salts are perfectly in line with those yielded by the three salts examined

previously. The close similarity of the crystal angles, the axial ratios, the volume constants, and the optical constants indicates that the ammonium salts of the double sulphate series are fully entitled to be considered as truly isomorphous with the corresponding potassium, rubidium, and cæsium salts. The ammonium salts do not, however, exhibit the eutropic relations which are found to exist between the salts of the three alkali metals. In spite of the departure of the ammonium and also the thallium salts from the law, which in the eutropic series expresses the connexion between the crystallographic properties and the atomic weight of the alkali metal, it has been clearly established that non-eutropic replacement may occur with extremely small alterations in the crystalline structure. These changes are almost vanishingly small when rubidium is replaced by either ammonium or thallium.

H. M. D.

Metallographic Study of the System Antimony–Tellurium. YASUKIYO KIMATA (*Mem. Coll. Sci. Kyoto*, 1915, **1**, 115—118. Compare Fay and Ashley, A., 1902, ii, 266).—The freezing-point curve of this system has a maximum at 620°, corresponding with the compound Sb_2Te_3. There are two eutectic points, at 540° and 28% Te and at 420° and 89% Te respectively. There is no indication of the formation of solid solutions. The flatness of the curve in the neighbourhood of the eutectic point on the bismuth side led Fay and Ashley to assume that solid solutions were formed on this side, the curve passing through a minimum. Microscopical examination confirms the existence of the two eutectics.

C. H. D.

Nitrogen Compounds of Gold. ERNST WEITZ (*Annalen*, 1915, **410**, 117—222).—Explosive nitrogenous compounds of gold are obtained not only from the salts or oxides of gold and aqueous ammonia or ammonium carbonate, but also from auric hydroxide and the ammonium salts of strong acids.

In 1840 Dumas assigned to the substance obtained from chloroauric acid and ammonia the formula

$$4(AuN,NH_3),2(AuCl,2NH_3),9H_2O,$$

and to another, prepared from auric hydroxide and ammonia, the formula $2(AuN,NH_3),3H_2O$. Raschig in 1886 regarded the latter as goldamidine, $NH\!:\!Au\cdot NH_2$; another compound, obtained from ammonia and an excess of chloroauric acid, was defined as goldiminochloride, $NH\!:\!AuCl$, whilst the former of Dumas' compounds was stated to be a mixture of these two.

These formulæ have been generally accepted without further evidence of constitution, and no attempt has hitherto been made to formulate the nitrogen compounds of gold in accordance with the co-ordination theory. The paper deals with these two points.

The compounds described by the author are generally obtained only under definite conditions of concentration of the reagents, and most of them have been analysed in the wet state on account of their explosiveness and decomposition by washing; the names are

determined by the ratio Au:N. From the numerous data recorded in the paper the following summary may be made. By treating an aqueous solution of chloroauric acid with ammonia (5 mols. or more), precipitates are obtained containing gold, nitrogen, and chlorine; as the amount of ammonia is increased the quantity of chlorine in the precipitate diminishes, the ratio Au:N, however, remaining constant at 1:1·5. These precipitates, which are called by the general name "explosive gold-chloride," are mixtures of two substances to which after drying the compositions $Au_2O_3,3NH_3$ (*sesquiammineauric oxide*) and $NH(AuCl{\cdot}NH_2)_2$ (*diaminoiminodiauric chloride*) are given. The chlorine-free constituent has been isolated. When air-dried it has the composition $2Au(OH)_3,3NH_3$ and is relatively harmless, but after drying at 105—110° or in a vacuum over phosphoric oxide it loses water and then explodes very violently by mere rubbing or pressure with a spatula.

Other mixtures (explosive gold-nitrate, -bromide, etc.) have been prepared by another method; the ratio Au:N is still 1:1·5.

When $N/5$-chloroauric acid containing ammonium chloride is added to a cold saturated solution of ammonium chloride saturated with ammonia, an individual compound, *diaminoauric chloride*, $Au(NH_2)_2Cl$, is obtained, which contains $1H_2O$. This is a dense, yellow powder, which is not explosive and is decomposed by washing with water, yielding ultimately a *substance*,

$$(?\ Au_3N_2,xH_2O \text{ or } 3AuO,2NH_3,yH_2O)$$

which is explosive.

Explosive gold-chloride and diaminoauric chloride are each converted by continued treatment with aqueous ammonia into sesquiammineauric hydroxide. This is changed to *diamminetriaurous oxide*, $\frac{3}{2}Au_2O,2NH_3$, a very explosive, black substance, by heating at 115—120°, and into a more explosive *monoammineauric oxide*, $Au_2O_3,2NH_3$, by hot water. Sesquiammineauric hydroxide is converted by warm dilute hydrochloric acid into chloroauric acid, explosive gold-chloride being an intermediate product. The hydroxide is scarcely attacked by dilute sulphuric or nitric acid in the cold, but by warming, ammonia is eliminated and explosive products (Au:N = 1:1) are obtained. Cold concentrated nitric or sulphuric acid does not decompose the sesquiammineauric hydroxide, a salt only being formed.

Tetra-ammineauric nitrate, $[Au(NH_3)_4](NO_3)_3$, colourless needles, is obtained when about $N/5$-chloroauric acid saturated with ammonium nitrate is added to a cold, saturated solution of ammonium nitrate, the mixture treated with gaseous ammonia at the ordinary temperature, and the precipitate washed with water. The salt can be crystallised from warm water. In not too dilute solution, it is precipitated unchanged by almost all nitrates, but with potassium, sodium, or ammonium nitrate in sufficiently concentrated solution it yields double nitrates,

$$[Au(NH_3)_4](NO_3)_3,MNO_3,$$

crystallising in needles. By double decomposition tetra-ammineauric nitrate has been converted into other salts containing the

cation $[Au(NH_3)_4]$ (represented by R in the formulæ; the *phosphate*, RPO_4,H_2O, finely crystalline, colourless precipitate; *oxalate nitrate*, $NO_3\cdot R(C_2O_4)$; *perchlorate*, $R(ClO_4)_3$, stout prisms (specially suited, by reaction with potassium salts, for the preparation of other soluble tetra-ammineauric salts); *oxalate perchlorate*, $ClO_4\cdot R(C_2O_4)$, very small leaflets; *chlorate*, $R(ClO_3)_3,2H_2O$, tufts of very thin, leafy needles; *iodate*; two *sulphate nitrates*, $NO_3\cdot R\cdot SO_4,H_2O$ and $R_4(SO_4)_5(NO_3)_2,2H_2O$; a complex *hydrogen sulphate*, $R_4H_5(SO_4)_4$; *sulphate perchlorate*; and *chromate*, $R_2(CrO_4)_3$, have been prepared. These salts are very stable in the solid state, and retain their ammonia even against the attack of concentrated acids. The salts of the strongest acids have a neutral reaction.

Tetra-ammineauric hydroxide has not been isolated, but its existence is indicated by the facts that the nitrate is distinctly more soluble in aqueous alkali hydroxides or ammonia than in water, and that from these alkaline solutions the nitrate is again precipitated by the rapid addition of nitric acid; when the alkaline solutions are kept they become brownish-yellow and yield yellow, explosive precipitates, which appear to be mixtures (explosive gold-nitrate, etc.) constituted similarly to explosive gold-chloride, or such mixtures containing also monoammineauric oxide.

Tetra-ammineauric salts of the halogen acids cannot be obtained, at all events in solution; when the colourless solution of tetra-ammineauric nitrate is treated with, for example, aqueous potassium chloride, a yellow colour is produced and a yellow, explosive precipitate (explosive gold-chloride nitrate) is obtained. Bromides, iodides, cyanides, and thiocyanates produce similar changes; potassium fluoride does not produce any coloration or precipitate.

Constitutional formulæ of the preceding nitrogen compounds of gold are discussed, and attempts are made to extend the formulæ to the explosive nitrogen compounds of other noble metals and of mercury. C. S.

Organosols of Metals and Metallic Hydroxides of the Platinum Group. III. CONRAD AMBERGER (*Kolloid Zeitsch.*, 1915, **17**, 47—51. Compare A., 1912, ii, 1053, 1059; 1914, ii, 60).—Colloidal osmium dioxide may be obtained by the method which has been used previously for the preparation of organosols of platinum and palladium. Lanolin is impregnated with a solution of potassium osmate and the mixture reduced by the addition of hydrazine hydrate. The product is dissolved in light petroleum, and can be precipitated by the addition of alcohol. It consists of colloidal osmium dioxide in admixture with lanolin as protective colloid. If the precipitated organosol is heated in a current of hydrogen at 50° to 60°, the oxide is reduced to metal, and the metallic organosol dissolves readily in ethyl ether, benzene, light petroleum, and other organic solvents. An organosol containing 21% of metallic osmium has been obtained in this way.

H. M. D.

The Hydroxylammonia Complexes of Bivalent Platinum. L. TSCHUGAEV and I. TSCHERNJAEV (*Compt. rend.*, 1915, **161**, 637—639).—The authors have succeeded in preparing all the members of the series of compounds $[Pt(NH_2{\cdot}OH)_n(NH_3)_{4-n}]Cl_2$, namely:

$$[Pt(NH_2{\cdot}OH)_4]Cl_2 \quad \text{(I.)} \qquad [Pt(NH_2{\cdot}OH)_3(NH_3)]Cl_2 \quad \text{(II.)}$$

$$\left[{OH{\cdot}NH_2 \atop OH{\cdot}NH_2}{>}Pt{<}{NH_3 \atop NH_3}\right]Cl_2 \quad \text{(IIIA.)} \qquad \left[{OH{\cdot}NH_2 \atop NH_3}{>}Pt{<}{NH_3 \atop NH_2{\cdot}OH}\right]Cl_2 \quad \text{(IIIB.)}$$

$$[Pt(NH_2{\cdot}OH)(NH_3)_3]Cl_2 \quad \text{(IV.)} \qquad [Pt(NH_3)_4]Cl_2 \quad \text{(V.)}$$

Of these, only I and V were previously known, and IIIB very imperfectly. Starting with Peyrone's chloride, this when digested with hydroxylamine in aqueous solution gives the compound IIIA, which yields the mixed *complex* ${NH_3 \atop Cl}{>}Pt{<}{NH_3 \atop NH_2{\cdot}OH}$, on treatment with hydrochloric acid at the temperature of a water-bath. This complex easily fixes two molecules of hydroxylamine to give the compound II, or two molecules of ammonia to give the compound IV. The compound IIIB is readily prepared by the action of hydroxylamine in aqueous solution on the chloride of Reiset's base II, the latter chloride being regenerated by the action of hydrochloric acid.

All the members of this series of compounds are colourless and more or less soluble in water, being ionised. The molecular conductivities lie between 240 and 260, which corresponds exactly with electrolytes of the type $(Pt,4A)X_2$. They yield platinochlorides, palladochlorides, and picrates. Of these, the platinochlorides, prepared by precipitation with potassium platinochloride, are the most characteristic, those of the compounds I, II, and IIIA being rose-violet in colour and those of IIIB, IV, and V being green. This reaction readily distinguishes between the isomerides IIIA and IIIB.

The chloride, $[Pt(NH_3)_3NH_2{\cdot}OH]Cl_2$, gives when heated with hydrochloric acid Cleve's salt, $(Pt,3NH_3,Cl)Cl$. W. G.

Mineralogical Chemistry.

The Occurrence of Nodules of Manganese in Mesozoic Deep-sea Deposits from Borneo, Timor and Rotti; their Significance and Mode of Formation. G. A. F. MOLENGRAAFF (*Proc. K. Akad. Wetensch. Amsterdam*, 1915, **18**, 415—430).—Analyses are given of nodules obtained from the island of Rotti,

where they occur in siliceous limestones, marls, and clay shales. I refers to a nodule from Sua Lain and II to a nodule found in the neighbourhood of Bebalain.

	SiO_2.	$Fe_2O_3+Al_2O_3$.	H_2O_2.	MnO_2.	CoO.	BaO.	CaO.	Na_2O.	H_2O.	CO_2.
I.	2·9	2·3	57·7	10·5	0·3	11·7	5·6	1·1	—	trace
II.	3·44	1·45	62·06	6·03	—	9·18	—	—	8·86	—

In the case of II, calcium oxide and alkalis were not estimated.

H. M. D.

Iron Ore on Calambayanga Island, Philippine Islands. WALLACE E. PRATT (*Philippine J. Sci.*, 1915, **10** *A*, 323—331).—The small island of Calambayanga, in the bay of Mambulao, south-eastern Luzon, contains a deposit of iron ore in metamorphosed sedimentary rocks, probably of Miocene age, which are intruded by andesites and overlie granite and diorite. The ore consists of almost pure hæmatite with only traces of magnetite, and is associated with some pyrites and quartz. Analysis I is of an average sample and II of a hand-specimen.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	MnO_2.	P.	S.	Total Fe.
I....	1·02	1·31	97·35	—	—	—	0·11	0·001	—	64·14
II....	1·29	6·52	68·28	9·22	2·77	0·29	0·09	0·10	0·12	54·94

L. J. S.

Iron Ore in Surigao Province, Philippine Islands. WALLACE E. PRATT and VICTOR E. LEDNICKY (*Philippine J. Sci.*, 1915, **10** *A*, 335—346).—The iron ores of the "Red Hills," on the north-eastern coast, consist of ferruginous (limonitic) clay covering the surface with a maximum thickness of about 20 metres. They are residual weathering products of igneous rocks (apparently peridotites), being of lateritic origin, and they resemble the clayey iron ores of Cuba. An analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	Cr_2O_3.	S.	P.	H_2O combined.	H_2O hygroscopic.	Total.
1·04	10·56	66·80	0·36	1·15	trace	trace	6·60	13·50	100·01

The average of numerous samples from bore-holes gives 47·40% Fe in the dehydrated ore.

L. J. S.

Ilvaite and other Minerals from Perda Niedda, Oriddese (Sardinia). ERNESTO MANASSE (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 285—289).—The ferriferous deposits of Perda Niedda contain a number of minerals, of which the following are described: (1) Ilvaite, which occurs in pitch-black, compact or radiating, fibrous masses, usually coated with ferric hydroxide, hardness about 6, D 3·95, composition as follows:

H_2O.	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Total.
2·66	29·37	0·67	19·47	27·74	6·48	13·25	0·51	100·15

(2) Garnet, usually dark green, but sometimes colophony-coloured, hardness 6—7, D 3·83, composition:

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	Total.
35·09	2·01	29·82	0·53	33·10	0·48	101·03

(3) Wollastonite, white, radiating, fibrous masses, hardness 4—5, D 2·86, composition:

H_2O.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Total.
0·85	50·49	Trace	0·54	47·72	0·51	100·11

T. H. P.

Analytical Chemistry.

Purification of Filter Paper by Hydrofluoric Acid. A. GAWALOWSKI (*Zeitsch. anal. Chem.*, 1915, **54**, 503).—Treatment of filter-paper with hydrofluoric acid results in the removal of silica, but any calcium and iron salts which may be present are converted into their respective fluorides; calcium fluoride is insoluble, and ferric fluoride is very slightly soluble in water, and although the latter may be removed by prolonged washing of the paper care must be taken that the wash-water is free from even traces of ammonium, potassium, or sodium salts, since these convert the ferric fluoride into a still less soluble double salt. The hydrofluoric acid solution used to remove the silica from the paper should be very dilute, and the paper should then be washed thoroughly; otherwise the paper becomes "hardened." W. P. S.

Use of the Colouring Substance of Red Cabbage as an Indicator. ECKERLIN (*Chem. Zentr.*, 1915, ii, 489—490; from *Mitt. K. Landesanst. Wasserhygiene*, 1915, 58—69).—A solution of the indicator is obtained by boiling red cabbage leaves for thirty minutes with three times their weight of water, filtering the extract, and, after cooling, neutralising it with $N/100$-potassium hydroxide solution. The indicator is green in alkaline solution and red in acid solution; at the neutral point, in the presence of alkali salts, the colour is bright blue, although the neutral indicator itself is violet. The indicator solution may be preserved by the addition of 0·2% of chloroform or 0·9% of phenol, and should be stored in the dark (compare A., 1913, ii, 237, 522). W. P. S.

Some New Indicators for the Colorimetric Determination of Hydrogen Ion Concentration. HERBERT A. LUBS and WILLIAM MANSFIELD CLARK (*J. Washington Acad. Sci.*, 1915, **5**, 609—617).—The authors have prepared and investigated a number of substances of the methyl-red type with the object of ascertaining their use for the estimation of the hydrogen-ion concentration in bacterial media. Among those newly prepared were: *monoethyl-red* [*ethylaminobenzene*-o-*azobenzoic acid*], which gives colour changes over the range P_H^+ 4·25—P_H^+ 6·00; *diethyl-red* (*diethylaminobenzene*-o-*azobenzoic acid*), colour changes over the range P_H^+ 4·50—P_H^+ 6·50; *monopropyl-red*, for the range P_H^+ 4·25—P_H^+ 6·25; and *dipropyl-*

red, for the range P_H^+ 4·50—P_H^+ 6·50. Of indicators already known, the following have been investigated to ascertain the range of concentration over which they may be used: monomethyl-red (P_H^+ 4·2—P_H^+ 6·3); α-naphthylamine-red (P_H^+ values of little use for the present purpose); dimethyl-α-naphthylamine-red (P_H^+ 4·50—P_H^+ 6·50); and diphenylamine-red (P_H^+ 4·25—P_H^+ 5·50). the symbol P_H^+ is defined as log. $1/C_H$, where C_H is the concentration of the hydrogen ion.

A number of indicators of the sulphone-phthalein type have been prepared by a new method and investigated. The method consists in the action of the phenol in question on the acid chloride of *o*-sulphobenzoic acid in the presence of zinc chloride. The following substances were prepared and the range of usefulness determined: phenolsulphonephthalein (P_H^+ 6·50—P_H^+ 8·50); *o*-cresolsulphonephthalein (P_H^+ values similar to those of the phenol compound); thymolsulphonephthalein (P_H^+ 8·0—P_H^+ 9·75); α-naphtholsulphonephthalein (P_H^+ 7·50—P_H^+ 9·00); tetrabromophenolsulphonephthalein (P_H^+ 3·50—P_H^+ 4·50); and bromothymolsulphonephthalein (P_H^+ 6·00—P_H^+ 7·25). Full details of the method of application of all the indicators mentioned are given in the paper. J. F. S.

Qualitative Micro-analysis. E. EMICH (*Zeitsch. anal. Chem.*, 1915, **54**, 489—502).—Directions and methods are given for the preparation of reagents used in micro-chemical tests and for the manipulation of precipitates, etc., in capillaries. The presence of nitrogen in 0·002 mg. of urea may be detected by heating this quantity of the substance with calcium carbonate and allowing the ammonia formed to come into contact with a minute fragment of red litmus paper contained in the capillary in which the mixture is heated; the ammonia may also be identified by means of its reaction with platinum chloride. A quantity of 0·0002 mg. of mercury can be detected by heating a drop of the solution containing the mercury with a piece of copper wire a few mm. in length and 0·1 mm. in diameter, then transferring the wire to a capillary, and subliming the mercury; the sublimed mercury may also be identified by converting it into the iodide. W. P. S.

Activation of Chlorate Solutions by Osmium. III. Separation of Hydrogen and Methane, Catalysis of Mixtures of Hydrogen and Oxygen. K. A. HOFMANN and OTTO SCHNEIDER (*Ber.*, 1915, **48**, 1585—1593. Compare A., 1913, ii, 62, 609).—The behaviour of various noble metals towards oxidisable gases in the presence of chlorate solutions has been studied. Preparations were made by evaporating the salts of the metals, in quantities equivalent to 1 gram of potassium osmate, to dryness with formic acid, and then adding a solution containing 15 grams of sodium chlorate and 2 grams of sodium hydrogen carbonate to 100 c.c. These mixtures were tested against the gases in a Hempel pipette. Towards hydrogen, the activity decreased in the order Pt, Rh, Ru, Pd, Au, Os, Ir, Ag, the highest absorption being only 18 c.c. in

twenty-four hours. Carbon monoxide was even less absorbed, the highest rate being 11 c.c. per day, and the order: Os, Rh, Au, Pt, Ru, Pd, Ir, Ag. Methane and ethylene were scarcely absorbed at all. The addition of an equimolecular quantity of osmium dioxide to these catalysts frequently gave a mixture that was much more active towards hydrogen or carbon monoxide than the two catalysts separately, this being particularly so in the case of palladium.

It has been the aim of the authors to improve the rate of absorption of hydrogen, so as to apply an activated chlorate solution in the estimation of hydrogen, and they have devised an absorbent which is prepared as follows: Tubes or rods of porous earthenware are steeped in 5% platinic chloride solution, then ignited in a flame so that they are covered with thin films of platinum, and packed into a Hempel pipette with the platinised ends uppermost. The pipette is then filled with a solution containing 35 grams of sodium chlorate, 5 grams of sodium hydrogen carbonate, 0·05 gram of palladous chloride, and 0·02 gram of osmium dioxide in 250 c.c. Such a mixture becomes more active after using it a time or two and can easily be arranged to absorb about 100 c.c. of hydrogen per hour without shaking, whilst the one quantity will oxidise slightly more than 22 litres. The cost of the soluble catalysts is only a few pence.

The contact "poisons" are usually removed before it is necessary to estimate hydrogen in a gaseous mixture, but, having done this, the above absorbent gives excellent results with pure hydrogen, and mixtures of hydrogen and methane, with or without nitrogen. Although oxygen alone is not absorbed, yet, when mixed with hydrogen, some of it takes part in the oxidation.

This has led to a study of the catalysis of mixtures of hydrogen and oxygen, that is, the oxidation of hydrogen under the influence of the above absorbent, with the difference that the chlorate was left out. Hydrogen alone is scarcely absorbed at all. The speed of the oxidation is influenced by the composition of the gaseous mixture, and is greatest, not with electrolytic gas, but with a mixture containing more hydrogen. Higher concentrations of oxygen have a bad, retarding effect, owing, no doubt, to an action on the catalyst, but this is overcome by diluting with nitrogen, or nitrogen and methane. That is, mixtures of hydrogen and air soon give the correct absorption, calculated for the gas which happens not to be in excess.

Carbon monoxide is much more slowly oxidised by the above combination of catalysts than hydrogen, but, strange to say, it does not "poison" the mixture, for this is just as useful for hydrogen after being treated with carbon monoxide as before. Neither does a change in the reaction of the solution affect the catalyst much, for phosphoric acid may replace the sodium hydrogen carbonate without changing the activity. J. C. W.

Estimation of Hygroscopic Moisture in Soils. W. D. Haigh (*Sci. Proc. Roy. Dublin Soc.*, 1915, [N.S.], **14**, 529—534).—The soil

is mixed with about three times its weight of calcium carbide and the acetylene evolved measured after a few minutes. The apparatus employed is similar to that described by Masson (T., 1910, **97**, 851).

The results obtained by this method were slightly lower than those obtained by heating the soil in an oven for sixteen hours. When much organic matter is present, as in peat, for instance, the difference between the two methods is greater, which seems to be due to the loss of volatile substances, other than water, when the soils are heated. Soil which was heated for several hours at 180° and then exposed to the air for several days gave results by the two methods agreeing within 0·04%.

It was found that 0·018 gram of water gives 10·5 c.c. of acetylene; the theoretical amount is 11·2 c.c. N. H. J. M.

Estimation of Total Chlorine in Caoutchouc Substitutes. A. HUTIN (*Ann. Chim. anal.*, 1915, **20**, 241—242).—From 0·2 to 0·5 gram of the substance is placed in a crucible, the latter is about one-half filled with a mixture of sodium carbonate and potassium nitrate, and then heated until gases burning with a luminous flame are no longer evolved and the mixture is melted. After cooling, the contents of the crucible are dissolved in dilute nitric acid and the chlorine is estimated volumetrically.

W. P. S.

Estimation of Fluorine. WILLIAM H. ADOLPH (*J. Amer. Chem. Soc.*, 1915, **37**, 2500—2515).—Practically the whole of the methods hitherto proposed for the estimation of fluorine have been subjected to a critical experimental examination. As the result of a large number of experiments it is shown that the Berzelius-Rose method of fusion of insoluble fluorides will give good results, and account for the whole of the fluorine in the mineral, if the residue insoluble in water after the first fusion is submitted to a second fusion. In studying the Offermann method, by which the fluoride mixed with silica is converted into silicon tetrafluoride which is decomposed by water and the solution titrated with alkali, it is shown that although the results are always low the best results are to be obtained by using 98·6% sulphuric acid at 200—220° and employing powdered quartz. The estimation of soluble fluorides is best effected by precipitation as lead chlorofluoride. The precipitate in this case is washed by means of a saturated solution of lead chlorofluoride. The only satisfactory method of detecting and estimating fluorine in small quantities is the colorimetric method of Steiger-Merwin. J. F. S.

Estimation of Oxygen by Winkler's Method. G. BRUHNS (*Chem. Zeit.*, 1915, **39**, 845—848).—The author discusses Winkler's modified method for the estimation of oxygen in waters (A., 1915, ii, 277), and suggests further manipulative simplification, such as keeping the potassium iodide in the solid form and adding a small crystal immediately before acidification, and conducting the titra-

tion in the original bottles after withdrawing a small measured volume to make room for the thiosulphate solution required for the absorption of the iodine. Also, in cases where nitrites or organic matter is present, instead of using carbon dioxide gas for converting the manganous hydroxide into carbonate, the addition of about 1·5 grams of solid potassium hydrogen carbonate is recommended. The precipitate rapidly settles, and the supernatant liquid can be removed, and the precipitate washed, without removal from the bottle, by decantation followed by upward filtration through a plug of cotton-wool placed in a fairly wide glass tube, at the upper end of which suction can be applied. Three rinsings with wash water are sufficient. G. F. M.

Determination of Gases Dissolved in Waters and Effluents. A. A. SWANSON and G. A. HULETT (*J. Amer. Chem. Soc.*, 1915, **37**, 2490—2500).—A method of determining the amount of gases dissolved in waters is described. This method is applicable in all cases, whether the water contains oxidisable material which would effect all titrimetric methods or for gases to which chemical methods are not applicable, for example, nitrogen. The method consists in principle in shaking a known volume of the water in a vacuum until the gas has distributed itself between the vacuum and the liquid and set up an equilibrium. This gas is then withdrawn to a gas analysis apparatus and analysed in the usual way. From the volumes of the water and vacuum and the partial pressures of the gas in equilibrium in the vacuum with that in the water, the total concentration of the gas originally present is calculated. In the case of oxygen a modification is introduced. A volume of water is shaken with a known volume of hydrogen, and the oxygen in the gas phase determined by passing the mixture over heated copper. Apparatus suitable for carrying out the above operations is described in detail in the paper. J. F. S.

Method for the Estimation of Inorganic Phosphorus in Body Tissues and Fluids. A. COSTANTINO (*Chem. Zentr.*, 1915, ii, 287; from *Arch. Farmacol. sperim.*, 1915, **19**, 307—316).—The substance or fluid is treated with acid mercuric chloride solution (see this vol., ii, 62), excess of mercury is removed as sulphide, the solution is neutralised, and treated with 25 c.c. of 10% barium nitrate solution and 12 c.c. of 10% ammonia. After twelve hours the precipitate is collected, washed with a solution containing 0·1% of barium nitrate and 0·1% of ammonia, then dissolved in dilute nitric acid, and the phosphoric acid estimated by the molybdic acid method. W. P. S.

Estimation of the Citric Acid Soluble Phosphates by the Ferric Citrate Method. N. ZACHARIADES and J. CZAK (*Chem. Zentr.*, 1915, ii, 724; from *Zeitsch. landw. Versuchs.-Wesen Oesterr.*, 1915, **18**, 472—475).—The authors consider Popp's method for the estimation of phosphates in Thomas slag to be preferable to the Darmstadt hydrochloric acid method, and to give more accurate

results. They point out that addition of hydrogen peroxide for the oxidation of any hydrogen, sulphide compounds is usually superfluous, and secondly that it is quite unnecessary to filter off the precipitate at once; it may without prejudice remain overnight. G. F. M.

Purification and Physiological Action of Animal Charcoal. A. G. Barladean (*Pharm. Zentr.-h.*, 1915, **56**, 683—687).—Animal charcoal usually contains impurities some of which are soluble in water and some in alkali or acid. Non-carbonised organic material is also frequently present. After re-carbonisation and repeated extraction with alkali, acid, and water, animal charcoal still retains salts which are sufficient to double or treble the growth of the rootlets of germinating wheat corns (*Triticum sativum*) immersed in distilled water and animal charcoal as compared with those immersed in distilled water alone. H. W. B.

Detection of Carbon Monoxide in Blood. Knud Sand (*J. Pharm. Chim.*, 1915, [vii], **12**, 366—368; from *Ann. hyg. pub. med. légale*, 1915, 222).—The suspected specimen of blood is compared spectroscopically with normal blood and with blood saturated with carbon monoxide. In each case 10 c.c. of a 3% dilution of the blood is taken and treated with about fifteen drops of a solution of iodine in potassium iodide, which transforms the hæmoglobin into methæmoglobin whilst the carbon monoxide-hæmoglobin remains unchanged. The solutions are then filtered and examined by the spectroscope. The author states that in this way 5% of carbon monoxide in blood can be detected. H. W. B.

Apparatus for the Transference of Gases used in Hesse's Method for the Estimation of Atmospheric Carbon Dioxide. Emil Grozea (*Chem. Zentr.*, 1915, ii, 297—298; from *Bul. Soc. Ştiinţe Bucureşti*, 1914, **16**, 156—159).—The air is originally contained in a holder supplied with a tap above and one below. The gas is displaced from this holder by water entering at the lower tap, and passes through the upper tap into a Hesse flask. This flask is originally filled with water, but as the air enters a corresponding amount of water flows out, the cork being doubly bored and fitted with tubes for this purpose. The carbon dioxide in the transferred air is then estimated by titration with barium hydroxide solution. D. F. T.

Estimation of Carbon Dioxide in Carbonates Decomposed by Ammonium Chloride Solutions. A. Cavazzi (*Ann. Chim. Applicata*, 1915, **4**, 137—144).—The carbonates of calcium, barium, strontium, magnesium, zinc, lead, cadmium, bismuth, copper, lithium, sodium, potassium, and probably other metals, are gradually decomposed and dissolved by boiling ammonium chloride solution, chlorides of the metals being formed and the carbon dioxide liberated as ammonium carbonate (compare A., 1915, ii, 795). The latter may then be passed into an ammoniacal calcium

chloride solution and the carbon dioxide estimated as calcium carbonate by titration with acid. This method is not affected by the presence in the carbonate of organic matter, and avoids the inconveniences caused by such impurities as hydrogen sulphide, sulphur dioxide, etc., sometimes contained in the gas liberated by acid from complex mixtures like cements. When the carbonate is insoluble in water the mixture containing it must be very finely powdered in an agate mortar; even with precipitated carbonates this treatment is recommended. The method has been applied to argillaceous limestone, cement, soil, ash, alkali carbonate, mixture of the latter with alkali hydroxide, white lead, bismuth carbonate, malachite, azurite, siderite, etc. T. H. P.

The Interaction of Perchloric Acid and Potassium Sulphate as an Example of Reversible Change. WILLIAM ALFRED DAVIS (T., 1915, **107**, 1678—1681).—It is shown that potassium may be accurately estimated by the perchlorate method even in presence of sulphates if the residual solution contains a sufficient excess of perchloric acid. If the evaporation is continued, so as to expel the greater portion of the perchloric acid, the precipitate is contaminated with hydrated potassium hydrogen sulphate

$$(KHSO_4,H_2O),$$

which increases the weight of the precipitate and thus leads to high results.

In general practice it is advisable, however, to eliminate the sulphate by evaporating with the addition of baryta, igniting very gently, and using the aqueous extract for evaporation with perchloric acid. The treatment with baryta removes not only sulphate, but also silica, magnesium, and phosphates. H. M. D.

The Estimation of Small Quantities of Potassium. A. J. HAMBURGER (*Biochem. Zeitsch.*, 1915, **71**, 415—463).—The principle of the method consists in the precipitation of the potassium in the form of the potassium sodium cobaltinitrite,

$$Co(NO_2)_3\cdot 3(K/NaNO_2),nH_2O,$$

which is then centrifuged and the volume of the precipitate is measured. The cobalt reagent is prepared by dissolving 50 grams of cobalt nitrite in 100 c.c. of water, to which solution 50 c.c. of glacial acetic acid is added. A second solution is made by dissolving 50 grams of sodium nitrite in 100 c.c. of water. Six parts by volume of the solution of the cobalt salt are mixed with ten parts by volume of the solution of sodium nitrite shortly before use. Five c.c. of the solution containing the potassium salt are mixed with 1·5 c.c. of the cobalt solution, and the mixture is kept for sixteen hours at 37°. It is then introduced into a special form of funnel (of which an illustration is given) which ends in a calibrated capillary tube of 0·04 c.c. capacity, etched in 100 parts, each of which corresponds with 0·001 gram of potassium. The precipitate is separated by centrifugalisation into this tube, and the volume is then determined. It is necessary to keep to the specified conditions of experiment to obtain satisfactory results, which are not

influenced by the presence of relatively large amounts of sodium, nor by the presence of calcium, magnesium, or sulphates. Phosphoric acid must, however, be removed, and for this purpose a mixture of calcium chloride and hydroxide or magnesia mixture can be best employed. Attention is called to the advantages of this method as compared with others that have been used for the estimation of potassium. S. B. S.

Estimation of Potassium in Fertilisers. FERDINAND PILZ (*Chem. Zentr.*, 1915, ii, 365; from *Zeitsch. landw. Vers.-Wesen Österr.*, 1915, **18**, 77—108).—The author has investigated the perchlorate method, and recommends the following procedure for the estimation of potassium in fertilisers: (A) *In potash fertilisers (potassium chloride, kainite, etc.).*—Ten grams of the sample are heated with 200 c.c. of water and 10 c.c. of concentrated hydrochloric acid; barium chloride solution is added in quantity sufficient to precipitate all the sulphate present, the mixture is cooled, diluted to 500 c.c., and filtered. Twenty-five c.c. of the filtrate are transferred to a glass basin, 10 c.c. of perchloric acid (D 1·125) are added, and the mixture is heated until hydrochloric acid vapours are no longer given off; after cooling, the contents of the basin are treated with 25 c.c. of alcohol containing 0·2% of perchloric acid, the precipitate is rubbed down to a fine powder, then collected in a Gooch crucible, washed with the acid alcohol, and dried at 120—130° for thirty minutes. The process must be carried out in an atmosphere free from ammonia vapours. (B) *In mixed fertilisers (superphosphates, wood-ash, etc.).*—Ten grams of the sample are dissolved, and the sulphate precipitated as described under (A); the solution is then rendered ammoniacal, heated, treated with ammonium carbonate, cooled, diluted to 500 c.c., and filtered. Fifty c.c. of the filtrate are evaporated in a platinum basin, the residue is dried and heated to expel ammonium salts, then dissolved in water, the solution filtered, and the potassium precipitated with perchloric acid as described (compare Davis, T., 1915, **107**, 678). W. P. S.

Determination of the Specific Electrical Conductivity in the Testing of Potable Waters. M. FORNAINI (*Ann. Chim. Applicata*, 1915, **4**, 150—182).—According to Kohlrausch, the amount of dissolved salts in an ordinary potable water is given, in mg. per litre, approximately by the expression $0·75 . \chi . 10^6$, where χ is the specific electrical conductivity of the water (compare Doroschevski and Dvorshantschik, A., 1913, ii, 1071).

The author's investigations in this direction show that the water should be freed from gas by thorough shaking prior to the measurement of the conductivity, and that care should be taken to avoid the formation on the electrode of gas bubbles, which may alter the capacity and thus lead to appreciable error. In order to avoid the use of a thermostat, the conductivity may be measured at any temperature between 0° and 25°, and the value corresponding with 18° calculated from the formula $\chi_{18} = \chi_t/[1+0·023(t-18)] = \chi_t . m_t$;

a table is given showing the value of m_t for each tenth of a degree between 0° and 25·9°. The proportions of organic matter normally present in natural waters have little influence on the conductivity, and the silicic acid, which varies from 0 to 0·1 gram per litre and may exist in the colloidal condition, usually introduces an error of from 0% to 4—5%, although in rare cases it may amount to 10%.

A number of waters from different parts of Italy have been examined, and the results indicate that 0·71 represents more nearly the average value of the coefficient of the above expression than Kohlrausch's value, 0·75. With the former number, the approximation of the calculated to the actual amount of salt present varies between −4·2% and 3·1%. Further, it is found that if the saline residue, calculated in mg. per litre according to Kohlrausch's expression (factor 0·75), is diminished by the number of mg. corresponding with the total hardness determined by Clark's method and expressed in French degrees, the resultant number differs from the actual salt content by from −3·9% to +2·1%.

When the value of $\chi_{18} . 10^6$ is less than 200, calculation of the saline residue from the conductivity gives somewhat untrustworthy results, since observational errors become appreciable at such dilutions, unless, indeed, special precautions are taken. Further, when $\chi_{18} . 10^6$ exceeds 700, anomalies become to increase in frequency and magnitude, owing to the diminished dissociation of the dissolved salts and the greater complexity of the salt solution; in these cases it is advisable to dilute the water with doubly distilled or conductivity water before measuring the conductivity.

A bibliography is appended. T. H. P.

Separation and Estimation of Aluminium and Glucinum by the use of Acetyl Chloride in Acetone. H. D. MINNIG (*Amer. J. Sci.*, 1915, [iv], **40**, 482—485).—The method of procedure is the same as that described for the separation of aluminium and iron (A., 1915, ii, 107), aluminium being precipitated from concentrated solution as the hydrated chloride and weighed as oxide, whilst glucinum remains in solution and is precipitated by ammonium hydroxide after diluting with water and warming on a steam-bath to volatilise the acetone. It is essential that the acetyl chloride be free from phosphorus compounds, and it is accordingly best prepared from acetic anhydride by saturating with hydrogen chloride and distilling at 100° in a rapid current of the same gas. The insolubility of glucinum chloride in the acetone–acetyl chloride mixture limits the process to the separation of quantities of the two elements which do not exceed the equivalent of 0·15 gram of the oxides, and of this amount glucinum should not greatly exceed one-third, otherwise there is a danger of inclusion of glucinum chloride in the aluminium precipitate. G. F. M.

The Development of Electro-Analysis in America. EDGAR F. SMITH (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 23—34).—Historical. A new method for the estimation of cobalt is described. The metal is converted into cobalt ammonium fluoride and electro-

lysed in a platinum dish with 0·8 ampere and 2 volts. The cobalt is precipitated completely on the anode as the dioxide in a hydrated form, which is weighed as Co_3O_4. The separation from nickel is complete. The addition of ammonium fluoride is equally successful.

C. H. D.

The Quantitative Estimation of Nickel with Dimethylglyoxime. KARL WAGENMANN (*Ferrum*, 1915, **12**, 126—129).—In place of weighing the dried precipitate of nickel dimethylglyoxime, the metal may be deposited electrolytically. The dimethylglyoxime may be added in hot aqueous solution, and the cold solution allowed to remain twenty-four hours before filtration. It is then washed with hot water, dissolved in dilute sulphuric acid, boiled with a few drops of hydrochloric acid and hydrogen peroxide to destroy the oxime, and neutralised with ammonia. After the addition of an excess of concentrated ammonia, the nickel is deposited on a gauze electrode at 70—80° in the usual manner for rapid analysis.

Manganese if present, as in the analysis of special steels, may be kept in solution by addition of ammonium chloride. C. H. D.

Action of Metallic Magnesium on Tin, Antimony, and Arsenic Sulphides. C. PERTUSI (*Ann. Chim. anal.*, 1915, **20**, 229—233).—When stannic sulphide is suspended in water and mixed with five times its weight of powdered magnesium it is reduced to stannous sulphide or metallic tin, and hydrogen sulphide is evolved. Arsenic sulphide, treated in a similar manner, gives at first a yellow solution, from which hydrochloric acid precipitates arsenious sulphide; if the reaction is prolonged, the whole of the arsenic may be removed from the solution. The addition of methyl alcohol tends to keep the arsenious sulphide in solution. Antimony sulphide reacts with magnesium in a similar way. The three elements, in admixture as their sulphides, may be detected as follows. A portion of the mixed sulphides is treated with magnesium powder, and the mixture filtered as soon as the yellow colour changes to brown; the brown residue is dissolved in hydrochloric acid and the heated solution treated with mercuric chloride, when a grey precipitate indicates the presence of tin. Another portion of the sulphides is shaken for a few minutes with magnesium powder and 5 c.c. of methyl alcohol, then heated slightly, and filtered. The filtrate is acidified with hydrochloric acid; if arsenic is absent, a slight precipitate of sulphur is obtained, but if arsenic is present, a yellow precipitate of arsenious sulphide is formed. A third portion of the precipitate is dissolved in concentrated hydrochloric acid, and a drop of 1% mercuric chloride solution and an excess of potassium hydroxide solution are added; a black turbidity indicates the presence of antimony. W. P. S.

Testing of Ores for the Cyanide Process. WELTON J. CROOK (*Chem. News*, 1915, **112**, 237—238; from *Chem. Engineer*, 1915, **21**).—To estimate the soluble acidity of ores, a portion of the

finely-ground sample is shaken for one hour with water, the mixture then filtered, and a portion of the filtrate titrated with standard sodium hydroxide solution, using phenolphthalein as indicator. The total acidity is estimated by shaking a definite quantity of the sample for six hours with 100 c.c. of the sodium hydroxide solution, filtering the mixture, and titrating the residual alkalinity with oxalic acid solution. The difference between the total acidity and the soluble acidity gives the "latent" acidity of the ore, that is, the acidity due to salts, sulphides, insoluble substances, etc. The quantities of the ore taken for the estimations and the strength of the alkali and acid solutions used are such that the results obtained, expressed in c.c. of the alkali solution, give directly the number of pounds of lime to be added to 1 ton of the ore to neutralise its acidity. W. P. S.

Differentiation of "Benzine" [Light Petroleum] and Benzene. HERM. MIX (*Kolloid Zeitsch.*, 1915, **17**, 7—9).—A resin extracted from dragon's-blood obtained from Sumatra is recommended for the differentiation of "benzine" and benzene. The resin has a deep red colour, and after treatment with hot petroleum (heavy and light) it is inactive towards "benzine" in the cold, but gives a deep coloration when acted on by benzene. The resin has been named dracorubin, and in the form of coloured test-papers it may be used for the approximate estimation of benzene in commercial samples of "benzine." The behaviour of dracorubin test-papers on treatment with various organic liquids (pure and commercial) has been examined in detail. H. M. D.

Physico-chemical Studies on Wines, Electrolytic Dissociation Constant of Wines. (MLLE.) CLELIA DI MAIO (*Ann. Chim. Applicata*, 1915, **4**, 245—268).—Measurements made on a series of ten wines give the following results: In genuine wines the process of electrolytic dissociation follows, with good approximation, the law of dilution. The dissociation constant, K, varies with different wines, but the variations lie within narrow limits; a means is thus furnished of determining adulteration with strong mineral acids. With nine wines the mean value of K was found to be $0{\cdot}0184 \pm 0{\cdot}0016$, with a probable error of 9·1%. Besides modifying considerably the value of the dissociation constant, the addition to wine of strong mineral acids in greater proportion than 0·05% effects an appreciable alteration in its degree of constancy owing to the prevalence of strong electrolytes which do not conform to the laws of dilution. Lack of constancy of K may also be observed in wines of low natural acidity which have been treated with metabisulphite. T. H. P.

Jaundice Produced by the Absorption of Picric Acid. Analysis of the Blood and Urine under this Condition. POGNAN and B. SAUTON (*J. Pharm. Chim.*, 1915, [vii], **12**, 350—352).—The picric acid is first extracted by ether or benzene from the urine or blood, and is then recognised by the usual tests. The results

show that there is not the slightest difficulty in distinguishing between pathological jaundice and the condition produced by the absorption of picric acid. H. W. B.

Recognition of Picric Acid in Urine in the Presence or Absence of Biliary Pigments. VILLEDIEU and MANCEAU (*J. Pharm. Chim.*, 1915, [vii], **12**, 366; from *Arch. med. pharm. milit.*, 1915, **64**, 255).—The method depends on the solubility of barium picrate and the insolubility of biliary pigments in the presence of salts of the alkaline earths. To 100 c.c. of urine are added about 20 c.c. of a saturated solution of barium chloride. The mixture is shaken, filtered, and the precipitate washed with 10—15 c.c. of boiling water. The filtrate and washings are treated with excess of sulphuric acid (about 5 c.c.), and, after removal of the precipitate, extracted twice with 20 c.c. of ether. After evaporation of the ether, the residue is dissolved in 2 c.c. of boiling water, filtered, and tested for picric acid in the following ways: (1) 2 drops of the liquid on a microscopic slide are mixed with 2 drops of a 10% solution of cocaine hydrochloride; tufts of silken crystals of cocaine picrate are observed under the microscope; (2) 10 drops of the liquid are mixed with 2 or 3 drops of alkaline potassium cyanide; a dark red colour appears on heating; (3) a piece of wool is dipped into 10 drops of the liquid diluted with water and heated on the water-bath; the wool is dyed yellow, and the colour is not removed by washing in water. H. W. B.

The Diphenylamine Reaction of Lævulose. LEOPOLD RADLBERGER (*Chem. Zentr.*, 1915, ii, 493; from *Österr.-ung. Zeitsch. Zucker-ind.*, 1915, **44**, 261—264. Compare A., 1912, i, 1020; 1913, i, 1386).—The author considers that the diphenylamine reaction of lævulose takes place in two stages; the diphenylamine is first converted by the concentrated sulphuric acid into diphenylbenzidine, and this is then oxidised by the lævulose into *N*-phenyldi-imine-*p*-diphenoquinone, an indamine. The blue colour reaction of carbohydrates described by Ihl (*Chem. Zeit.*, 1885, **9**, 451) with diphenylamine is probably due to the fact that carbohydrates yield lævulose and dextrose when heated at 68°, and that both the latter act as oxidising substances. W. P. S.

Action of Copper Solutions in Sucrose. Estimation of Invert-sugar in the Presence of Sucrose. ÉMILE SAILLARD (*Compt. rend.*, 1915, **161**, 591—593).—In estimating invert-sugar in the presence of sucrose by the reduction of alkaline copper solutions the results obtained are always too high, owing to a portion of the sucrose being attacked and then exerting a reducing action. This attack is more marked the more alkaline is the copper solution, and it varies with the amount of invert-sugar present. The author advises the use of a solution containing 69·26 grams of copper sulphate per litre, and a solution containing 346 grams of Rochelle salt and 130 grams of sodium hydroxide per litre. Ten c.c. of each of these solutions are mixed and heated for twenty-two minutes

with 50 c.c. of the prepared sugar solution at 62—64°. The blue filtrate from this estimation is similarly heated for a further twenty-two minutes, and if this second heating precipitates less cuprous oxide than the first, the sugar solution contains reducing sugars. A table is given for calculating the results. W. G.

Action of Sucrose on the Alkaline Copper Solution. L. MAQUENNE (*Compt. rend.*, 1915, **161**, 617—623. Compare Saillard, preceding abstract).—Working with Barreswill's alkaline copper tartrate solution the author finds that, with sucrose, the amount of reduction increases rapidly with the concentration of the copper and the time of heating for a given concentration of sucrose. The reduction is apparently not due to a preliminary inversion of the sugar, but to a direct oxidation of the sugar, accompanied, or followed possibly, by hydrolysis. As the concentration of the sugar solution increases, the amount of cuprous oxide produced at first increases rapidly to a maximum and then slowly decreases. This maximum effect is reached when the concentration of the sucrose with respect to the total volume of solution is about 11%. It is probable that complex copper and potassium sucrates are formed, the dissociation of which diminishes in the presence of the excess of sucrose, thus reducing the alkalinity and active copper content of the liquid. The presence of invert-sugar acts in the same way as an excess of sucrose, causing a diminution in the reduction due to the sucrose. W. G.

New Method for the Estimation of Fatty Acids in Soaps. H. F. SLACK (*Pharm. J.*, 1915, **95**, 696—697).—Five grams of the soap are heated with 10 c.c. of glycerol until the soap has dissolved; the mixture is then acidified with 4 c.c. of hydrochloric acid (1 : 3), and the liberated fatty acids are drawn up into a graduated 5 c.c. pipette; hot water is added, if necessary, to bring the whole of the fatty acid into the pipette. The top of the latter is now closed and the pipette suspended in a water-bath at 55°. The volume of the fatty acids is read at this temperature; the volume multiplied by the sp. gr. gives the weight. It is necessary, for this purpose, to know the sp. gr. of the fatty acids of the more common classes of soaps, and these numbers should be determined at 55°. The use of glycerol for dissolving the soap has the advantage that the liberated fatty acids form a perfectly clear layer above the layer of glycerol, etc. W. P. S.

Detection of Lactic Acid in Leathers, and also in Tanning Lyes and Other Liquids. R. LAUFFMANN (*Chem. Zentr.*, 1915, ii, 763—764; from *Ledertech. Rundschau*, 1915, **14**, 264—268, 287—292).—Lactic acid may be detected by conversion into acetaldehyde by distillation with lead peroxide. If the solution under examination is very dilute, it must first be concentrated by evaporation with the addition, if sulphate or chloride be present, of 10 c.c. of 10% sodium carbonate solution, the equivalent quantity of sulphuric acid being again added before the distillation. Twenty-

five c.c. of the prepared solution are distilled in a 500 c.c. flask with 3 grams of lead peroxide at such a rate that about 40 drops are collected per minute. In the distillate, which is collected in 5 c.c. fractions, the acetaldehyde is detected by adding 10—12 drops of an aqueous diethylamine solution (2 drops in 25 drops of water) and 5—6 drops of a 0·08% solution of sodium nitroprusside. In presence of acetaldehyde the blue colour which appears in one to two minutes persists, according to the amount present, for from one to fifteen minutes after the distillation is complete; otherwise it rapidly fades during the distillation. The presence of acetaldehyde may also be detected by the iodoform reaction. About 8 drops of 10% solution of iodine in potassium iodide and sufficient sodium hydroxide to decolorise is added to the distillate, and a distinct cloudiness after some minutes is conclusive of the presence of acetaldehyde ,which may be further confirmed by warming the alkaline solution with a little resorcinol when a carmine-red coloration is produced and the odour of iodoform becomes still more apparent. G. F. M.

Detection of Free Mineral Acids and Lactic Acid in Leather. R. LAUFFMANN (*Chem. Zentr.*, 1915, ii, 765; from *Ledertech. Rundschau*, 1915, **8**, 292—301).—Dried and undried portions of the leather are dialysed; if the former dialysate is acid, mineral acids or oxalic or lactic acids may be present. If only the latter dialysate is acid, the acidity is due to volatile organic acids. In the former eventuality an extract of 20—30 grams of the leather in 200 c.c. of hot water is tested for sulphate, chloride, and oxalic acid ions. If the latter is present, the question as to whether the leather contained free mineral acid cannot be decided. If absent, lactic acid is tested for in an extract of the finely divided leather prepared by prolonged digestion at 60—65° by the author's method (preceding abstract). If both oxalic and lactic acid are thus proved absent, the sulphate and chlorine ions must have been present as free acid. In this case the dialysing process can be utilised for their quantitative estimation, the aqueous dialysate being titrated with $N/10$-alkali hydroxide, using Congo-red as indicator. G. F. M.

Estimation of Total Tartaric Acid, Calcium Tartrate, Potassium Hydrogen Tartrate, and Free Tartaric Acid in Wine. RUDOLF KUNZ (*Chem. Zentr.*, 1915, ii, 287—288; from *Arch. Chem. Mikroscopie*, 1915, No. 3).—Fifty c.c. of the wine are treated with exactly 3 c.c. of $N/2$-hydrochloric acid and 2 c.c. of 20% potassium chloride solution, and evaporated to 10 c.c. Another portion of 50 c.c. of the wine is evaporated at the same time, without any addition, until the residual solution weighs 10 grams. To each of the residual solutions are now added 100 c.c. of 96% (by vol.) alcohol; after twelve hours the precipitates are collected, washed with alcohol, then dissolved in hot water, and the .solutions titrated with $N/10$-alkali solution. The quantity of the total tartaric acid and of the potassium hydrogen tartrate in the wine is thus

obtained. The filtrate from the potassium hydrogen tartrate estimation (the precipitate also contains the calcium tartrate) is now treated with 2 c.c. of 20% potassium chloride solution; after twelve hours, 2 c.c. of *N*/10-hydrochloric acid are added, the precipitate is collected, washed with alcohol, dissolved in hot water, and the solution titrated. This result gives the amount of free tartaric acid present, and the difference between the quantity of total tartaric acid and the sum of the quantities of free tartaric acid and that present as potassium hydrogen tartrate gives the amount present as calcium tartrate. W. P. S.

Source of Error in the Estimation of Tartaric Acid in Wine Lees and Tartars. P. CARLES (*Ann. Chim. anal.*, 1915, **22**, 240—241).—When the Goldenberg method (A., 1908, ii, 237) is employed for the estimation of tartaric acid in tartars, etc., containing calcium carbonate, the weighed portion of the substance should be mixed with twice its weight of water and then treated with hydrochloric acid, in small quantities at a time, until the mixture no longer evolves carbon dioxide when the acid is added. Eighteen c.c. of hydrochloric acid (D 1·10) are now added, and the process carried out as described. Unless the calcium carbonate is first decomposed, the quantity of hydrochloric acid added subsequently may not be sufficient to dissolve the tartrates. W. P. S.

Estimation of Acidity in Potatoes. J. F. HOFFMANN and FR. PRECKEL (*Landw. Versuchs-Stat.* 1915, **87**, 237—239).—The expressed potato sap (50 c.c.) is diluted to 250 c.c. with 95% alcohol, frequently shaken during an hour, and filtered. Of the filtrate, 100 c.c. are diluted with 100 c.c. of water, vigorously shaken to expel carbon dioxide, and titrated in presence of 1 c.c. of rosolic acid. A titration is also made, in a similar vessel, in a mixture of alcohol (80 c.c.) and water (120 c.c.), and the result deducted from that obtained with the potato sap.

It is of importance to employ solutions containing the same relative amounts of water and alcohol; with greater proportions of alcohol, the change of colour is retarded. N. H. J. M.

The Salicylates. II. Methods for the Quantitative Recovery of Salicyl from Urine and other Body Fluids. T. W. THOBURN and PAUL J. HANZLIK (*J. Biol. Chem.*, 1915, **23**, 163—180).—The term "salicyl" is employed to indicate the salicyl group in whatever form it occurs. To recover salicyl from urine, the fluid is distilled in the presence of syrupy phosphoric acid (20 c.c. of 80% acid solution to 100 c.c. of urine). By this means the conjugated salicylates, such as salicyluric acid, are hydrolysed, and the salicylic acid distils over with the steam. The amount is then estimated colorimetrically in an aliquot part of the distillate by the addition of 2% ferrous ammonium sulphate, the colour produced being estimated by comparison with solutions containing varying amounts of a standard solution, of which 1 c.c. contains 0·0001 gram of salicylic acid. To estimate salicyl in blood, the free salicylic acid

is extracted with ether, and the amount estimated colorimetrically. To estimate the conjugated salicyl, the proteins are first removed by addition of ten times the volume of alcohol; to an aliquot part of this liquid a few drops of saturated zinc chloride solution are added and the mixture is boiled. The filtrate is then freed from alcohol by boiling, and the aqueous solution is hydrolysed by phosphoric acid, and the estimation completed by the method described above in the case of urine. A method is also suggested for the estimation of salicyl in fæces. S. B. S.

Biochemical Reaction of Rancid Fats. J. VINTILESCO and ALIN POPESCO. (*J. Pharm. Chim.*, 1915, [vii], **12**, 318—323).—The rancidity of fats and oils is due to the fixation of oxygen, and the authors show that this oxygen may be liberated by the action of peroxydase and detected by the guaiacum reaction. Ten grams of the fat are just melted in a test-tube, 5 drops of diluted blood or of 3% hæmoglobin solution are added, followed by 10 drops of guaiacum tincture and 10 c.c. of water, and the mixture is shaken for one minute. If the fat is rancid, the emulsion is coloured blue, the intensity of the coloration depending on the degree of rancidity, whilst in the case of non-rancid fats, or oils, the mixture remains colourless. The blue coloration may be rendered more distinct when dealing with fats which are only slightly rancid by adding an equal volume of 95% alcohol to the mixture after the latter has been shaken. That the acidity of a fat is not a function of the rancidity is shown by the fact that a rancid acid fat, after being neutralised and washed with water and alcohol, gives a reaction equal in intensity to that yielded by the fat before neutralisation. Rancid fats still give the reaction after being heated at 120° for a few minutes, but not after being heated at 200°.

W. P. S.

Applied Plant Microchemistry. XI. Microchemical Detection of Baptisin in Baptisia Tinctoria (Roots). O. TUNMANN (*Chem. Zentr.*, 1915, ii, 288—289; from *Apoth. Zeit.*, 1915, **30**, 272—274).—Pyridine is a better solvent than dilute alcohol for the extraction of baptisin from the powdered roots of *Baptisia tinctoria* (wild indigo); after repeated crystallisations from dilute alcohol, the glucoside is obtained as a white, crystalline powder, m. p. 244°. It is soluble in aniline, pyridine, amyl alcohol, and potassium hydroxide solution, insoluble in ethyl acetate and turpentine, and slowly soluble in chloral hydrate solution and acetic acid. Baptisin may be detected in sections of the root by treating the section with vanadium sulphate; the edge of the section exhibits a violet coloration which changes to light blue; cerium sulphate and tungsten sulphate yield reddish-violet colorations. Baptisin sublimes for the greater part without decomposition. If 5 mg. of the powdered root are heated, the first sublimate obtained consists of colourless or light yellow needles of the glucoside; the subsequent sublimate consists of white prisms of baptigenin. The glucoside and its derivative give a red coloration with vanadium

sulphate, the colour changing gradually to violet and brownish-blue. When the sublimate is treated with a drop of sulphuric acid and a crystal of tungstic acid is added, the edges of the crystal show a deep violet coloration. If the sublimate is mixed with iodic acid solution, dried, the residue washed with water and then treated with sulphuric acid, the crystals become red, then violet or black, and dissolve, whilst the edge of the sulphuric acid exhibits a bluish-grey colour. Baptisin is localised in the parenchyma.

W. P. S.

A Frangula Substitute, the Barks of Rhamnus Carniolica and Alnus Glutinosa. O. TUNMANN (*Chem. Zentr.*, 1915, 674; from *Schweiz. Apoth. Zeit.*, 1915, **53**, 313—318; 325—332).—A proposed substitute for frangula consists of a mixture of 15% of the bark of *Rhamnus carniolica* and 75% of the bark of *Alnus glutinosa.* The former bark contains both free and combined hydroxymethylanthraquinones and might serve as a substitute for frangula, but the bark of *Alnus glutinosa* is worthless. The three *Rhamnus* drugs may be distinguished by the rays in the cambium layer; in the case of frangula they form one or two, very seldom three, layers; in *R. purshianus* they appear in one to three, seldom four, layers; in *R. carniolica* they are in four, six, or even eight, layers. *R. carniolica* contains 1·84% of free, and 3·78 of combined, hydroxymethylanthraquinones; frangula-emodin is also present, but not chrysophanic acid. The total anthraquinones in *R. carniolica* may be estimated as follows: Five grams of the dry powder are boiled with 100 grams of dilute sulphuric acid for thirty minutes under a reflux apparatus, the mixture then filtered, and the filtrate extracted twice with chloroform (50 and 20 grams). The chloroform solution is shaken for fifteen minutes with two quantities of 50 grams of 5% sodium hydroxide solution, the alkaline extract is acidified with hydrochloric acid, the precipitated hydroxymethylanthraquinones collected, dried at 100°, and weighed. W. P. S.

Identification and Estimation of "Saccharin" [*o*-Benzoicsulphinide] in Foodstuffs. FEDERICO CECCHERELLI (*Boll. chim. farm.*, 1915, **54**, 641—648).—Before a foodstuff is treated with ether in order to extract any "saccharin" present, it is necessary that alcohol should be completely removed, since even a small residuum of alcohol may result in the extraction of other sweet substances, such as glycerol, lævulose, various glucosides, etc. In some cases the whole of the alcohol is not expelled by a single evaporation, and it is advisable repeatedly to take up the residue in distilled water and evaporate. The residue obtained after extraction with ether and expulsion of the latter should be purified by treatment with permanganate, and should then: (1) be pronouncedly sweet; (2) give the reaction for salicylic acid only after fusion with sodium hydroxide at 250°; (3) contain sulphur in the theoretical proportion; (4) yield a silver derivative containing 37% of the metal; (5) give Tarugi and Lenci's reaction (compare A., 1912, ii, 397) after hydrolysis by means of sulphuric acid. T. H. P.

The Microchemical Method for Gasometric Determination of Aliphatic Amino-nitrogen. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1915, **23**, 407—409. Compare A., 1910, ii, 751; 1911, ii, 164; 1912, ii, 1008; 1913, ii, 1084).—A modification of the gas-burette employed for measurement of the nitrogen is described. This is of 3 c.c. capacity, graduated into divisions of 0·01 c.c. placed 1 mm. apart. The zero point is placed a few millimetres below the stop-cock. Readings to 0·001 c.c. are possible. A modification in the manipulation of the author's micro-method is also described.

S. B. S.

The "Ninhydrin" Reaction. VICTOR JOHN HARDING (*Trans. Roy. Soc. Canada*, 1915, **9**, 33—42).—A critical examination of the conditions governing Ruhemann's test for amino-acids with triketo-hydrindene hydrate (T., 1910, **97**, 2025). The author finds that under accurately defined conditions of concentration and temperature the test can become specific for amino-acids, these being the only substances which give the test readily and clearly in very dilute solution. He recommends that, in testing for amino-acids, not more than 0·1 mg. of nitrogen be present in each c.c. of the liquid to be tested, and that 1 c.c. of it should be heated in a boiling water-bath with 1 c.c. of a 1% solution of "ninhydrin" for fifteen minutes. Evaporating the liquid to be tested to dryness in a dish with the reagent is unsatisfactory. In the presence of pyridine, ammonium salts and primary amines, as well as amino-acids, react strongly with triketohydrindene hydrate, and therefore the colorimetric method of Harding and MacLean for estimating the nitrogen in α-amino-acids present is inapplicable to the analysis of physiological fluids (compare A., 1915, ii, 382). The blue coloration obtained by Halle, Loewenstein, and Pribram with this reagent and glycerol and allied substances (compare A., 1913, ii, 922) is shown to be due to the presence of traces of nitrogenous impurity. The blue colour obtained with amino-acids is characterised in three ways, namely, (1) It gives a broad absorption band in the visible spectrum extending from the red into the green part of the spectrum when viewed in dilute solution; (2) the blue colour changes to purple when viewed in artificial light; (3) the colour is resistant to mild oxidation, the passage of a rapid current of air for five minutes through a standard colour having no effect on the quantity present. The blue colour given by hydrindantin and potassium or sodium hydroxide differs from this very markedly in that it gives no absorption band in the visible spectrum; it remains blue when viewed by artificial light, and it is very readily oxidised to a colourless solution when shaken with air. W. G.

New Reaction of *iso*Thiocyanates. G. DENIGÈS (*Bull. Soc. chim.*, 1915, [iv], **17**, 380—381).—To a few c.c. of the solution to be tested twice its volume of a solution of mercuric sulphate (28 grams per litre) is added, the mixture shaken, filtered, if necessary, and heated in a boiling water-bath for one to five minutes, according to the dilution. *iso*Thiocyanates, if present to the extent of 0·25 gram per litre, will give a crystalline precipitate of dithio-

trimercuric sulphate (compare A., 1915, ii, 835, 839), which can be examined under a microscope and characterised. W. G.

Mercury Ureometer of Simple Construction. HENRI MARTIN (*J. Pharm. Chim.* 1915, [vii], **12**, 352—354).—A modification of Esbach's ureometer is described for the estimation of urea in the blood. The blood is treated with an equal volume of a 20% solution of trichloroacetic acid, and the urea in a measured volume of the filtrate decomposed by sodium hypobromite. The nitrogen gas evolved is collected in the modified Esbach's ureometer over mercury. H. W. B.

Method for the Extraction of Creatine and Creatinine from Body-tissues and Fluids. A. COSTANTINO (*Chem. Zentr.*, 1915, ii. 287; from *Arch. Farmacol. sperim.*, 1915, **19**, 254—258).—The fluid, or the finely-divided organ, is shaken for two hours with 200—250 c.c. of 2% mercuric chloride solution containing 1% of hydrochloric acid; the mixture is then filtered, and the excess of mercury is removed as sulphide. An aliquot portion of the solution is heated to expel hydrogen sulphide, neutralised with sodium hydroxide, and concentrated to about 10 c.c. The solution thus obtained is colourless and free from proteins, and serves for the colorimetric estimation of the creatine. W. P. S.

The Use of Trichloroacetic Acid as a Protein Precipitant. I. GREENWALD (*J. Amer. Chem. Soc.*, 1915, **37**, 2604—2605).—The author disclaims any right to the discovery of the general use of trichloroacetic acid as a reagent for proteins (compare Graves and Kober, *ibid.*, 2445). D. F. T.

Analysis of Proteins by Determination of the Chemical Groups Characteristic of the Different Amino-Acids. A Correction. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1915, **23**, 411).—The formula for determination of histidine and arginine given in the original paper (A., 1911, ii, 944) should read: Histidine $=\frac{3}{2}(D-\frac{3}{4}\text{Arg}) = 1\cdot5D - 1\cdot125\,\text{Arg}$, instead of Histidine $\text{N} = 1\cdot667D - 1\cdot225\,\text{Arg}$. as there given. D = diamino-acid nitrogen, Arg. = arginine nitrogen. S. B. S.

The Proteins in Caoutchouc and in Caoutchouc Latex. FR. FRANK (*Chem. Zentr.*, 1915, i, 1345; from *Gummi-Zeit.*, 1914, **29**, 196—198).—The following method is recommended for the separation of the nitrogenous substances in crude caoutchouc. From 1 to 2 grams of the sample are mixed in a test-tube with 30 c.c. of cumene, limonene, or dipentene, and the mixture is boiled under a reflux apparatus until a homogeneous solution is obtained. The tube and its contents are then submitted to centrifugal action (2500—3000 revs. per minute) for one to one and a-half hours, the clear liquid is decanted, the sediment next boiled with xylene, and again submitted to centrifugal action, and these operations are repeated, using light petroleum and ether, respectively, as the

solvents. The residue is then dried, weighed, and further examined. It yields distinct reactions with the biuret and xanthoprotein tests, with Millon's reagent, and in most cases the presence of tyrosine can be detected. The substance responds to all the precipitation tests for proteins. The cleavage products obtained when the substance is hydrolysed completely are the same as those obtained from the latex and from the serum after coagulation. The presence of the following products may be detected: monoaminomonocarboxylic acids, aromatic amino-acids (phenylalanine, tyrosine), heterocyclic amino-acids (tryptophan), diaminomonocarboxylic acids, monoaminodicarboxylic acids, and cystine. It follows that, in working up latex, the proteins should be separated simultaneously with the caoutchouc in such a way that they do not undergo further decomposition. W. P. S.

Estimation of the Ammonia from the Amino-acids and Proteins of Urine by Means of Formaldehyde. M. W. Scheltema (*Pharm. Weekblad.*, 1915, **52**, 1549—1555).—A historical survey of the application of formaldehyde to the estimation of combined ammonia in urine, and an account of the results obtained by the author by this method. A. J. W.

Acid Ratio: A New Method for Estimating the Proteolytic Strength of Germinated Grain in Technical Analysis. Carl A. Nowak (*J. Ind. Eng. Chem.*, 1915, **7**, 858—859).—The method is based on the formaldehyde titration of the amino-groups. Fifty grams of finely-ground malt are shaken for thirty minutes with 150 c.c. of cold water, and the mixture then filtered, the first portions of the filtrate being returned to the filter. Exactly forty-five minutes after starting the extraction, or fifteen minutes after removing the mixture from the shaking machine, 20 c.c. of the filtrate are transferred to a beaker, 20 c.c. of water and 0·5 c.c. of 0·5% phenolphthalein solution (in 50% alcohol) are added, and the solution is titrated with $N/10$ sodium hydroxide solution. This titration gives the natural acidity. To the mixture are now added 10 c.c. of 40% formaldehyde solution (previously mixed with 5% of its volume of 0·5% phenolphthalein solution and then neutralised), and the titration is continued until a distinct pink coloration is obtained. This second titration is a measure of the amino-groups present. The ratio between the amino-acidity and the natural acidity, obtained by dividing the number of c.c. of alkali solution representing the amino-acids by the number of c.c. representing the natural acidity, is as 1 : 1 or greater. This ratio is termed the acid ratio of malt. A really good malt should be high in natural acidity and should show an acid ratio of 1 : 1·10, which may be expressed as 110; in some malts it may be as high as 130. To obtain comparative figures as to the proteolytic strength of different malts, the remainder of the filtrate is maintained at the ordinary temperature for sixteen hours, and a second estimation of the acid ratio is then made. Malts showing the greatest increase in the acid ratio are those having the greatest

peptic strength; the increase may amount to from 5 to more than 30 units. W. P. S.

Analysis of Soils with Strong, Hot Hydrochloric Acid. D. J. Hissink (*Bied. Zentr.*, 1915, **44**, 367—369; from *Internat. Mitt. Bodenk.*, 1915, **5**, 1).—Whilst the amount of acid, per gram of soil, and the duration of the boiling do not vary much in the method usually employed, there seems to be less uniformity as regards the strength of the acid, and hence the temperature, which depends on the density of the acid. The following method is proposed. The soil (10 grams) is first treated with water or dilute acetic acid to remove any acid or carbonates. It is then boiled for a few minutes in an open flask with hydrochloric acid (about 25%) until the temperature 110° is reached, after which it is boiled for two hours in a reflux flask. N. H. J. M.

Method for the Estimation of the Immediate Lime Requirements of Soils. W. H. MacIntyre (*J. Ind. Eng. Chem.*, 1915, **7**, 864—867).—There is a considerable difference between a soil's ability to decompose immediately calcium carbonate and its power of continuing the decomposition when the soil and an excess of calcium carbonate remain in moist contact. In certain lime-treated plots, 35% of the accumulated lime after thirty-two years' treatment was found to be present as silicate. The method described deals with the immediate lime requirement. From 5 to 10 grams of the soil are mixed with 150 c.c. of calcium carbonate solution (see below) and evaporated to a paste; the latter is then washed into a flask with 60 c.c. of water free from carbon dioxide, the carbon dioxide is liberated with phosphoric acid and absorbed in a definite volume of $N/2$ sodium hydroxide solution. The amount of sodium carbonate formed is estimated either by the double titration method or by adding barium chloride and titrating the alkali hydroxide after the barium carbonate has settled. The calcium carbonate solution employed is prepared by passing carbon dioxide for four hours into 4 litres of water containing 20 grams of calcium carbonate in suspension, then filtering the solution and storing it under pressure of carbon dioxide. The difference between the calcium carbonate content of the 150 c.c. of this solution employed and the residual calcium carbonate found in the actual estimation is a measure of the calcium carbonate decomposed by the soil. W. P. S.

General and Physical Chemistry.

The Double Refraction of Vanadium Pentoxide Solution. H. DIESSELHORST and H. FREUNDLICH (*Physikal. Zeitsch.*, 1915, **16**, 419—425).—The anisotropy exhibited under certain conditions by a colloidal solution of vanadium pentoxide has been further investigated. If the sol is allowed to flow through a tube the axis of which is parallel to the line connecting crossed Nicols placed at opposite ends of the tube, the field of view is illuminated in convergent light, and shows the cross and concentric rings which are observed when the light passes through a plate of a uniaxial crystal cut perpendicularly to the axis. By the use of a quarter-wave mica plate it is found that the streaming sol behaved like a positive uniaxial crystal.

If a concentrated colloidal solution is made to flow through a tube of triangular cross-section which is used as a prism, it is found that the red line of hydrogen is resolved into two oppositely polarised lines. The more strongly refracted ray has its vibrations parallel to the direction of flow and therefore parallel to the major axes of the colloidal particles, and in accordance with Babinet's rule, this extraordinary ray is more strongly absorbed than the other.

Some of these effects have also been observed, although less clearly, with an old ferric hydroxide solution. The properties of such sols are obviously similar to those shown by crystalline liquids, and in this connexion the general question of the anisotropy of the amorphous state is discussed. H. M. D.

The Arc- and Spark-spectrum of Silver in International Normals. JOSEPH FRINGS (*Zeitsch. wiss. Photochem.*, 1915, **15**, 165—182).—Accurate measurements of the wave-lengths of lines in the arc and speck spectra of silver have been made by the use of a large concave grating. The data are compared with the results of previous observers, and the series relations exhibited by certain pairs of lines are discussed. H. M. D.

Changeable Lines in the Arc Spectrum of Iron. JOSEPH LANG (*Zeitsch. wiss. Photochem.*, 1915, **15**, 223—252).—According to the measurements of Goos (A., 1912, ii, 404, 1016), the wave-lengths of certain lines in the arc spectrum of iron vary to an appreciable extent with the length of the arc which is employed as the source of the radiation. In view of the importance of this result in connexion with the determination of the wave-lengths of secondary and tertiary normal lines in the iron arc spectrum, further experiments have been made in order to ascertain more exactly the relation between the wave-length and the conditions of the arc discharge.

Observations were made with short (2—4 mm.) and long (9—16

mm.) arc; the strength of the current was varied from 3 to 15 amperes and the applied potential from 60 to 440 volts. In the case of the long arc, series of measurements were also made with the light emitted in the neighbourhood of the anode and of the cathode.

The data obtained from observations in the greenish-yellow region (λ 5360 to λ 5660) show clearly that the wave-length of a large number of lines varies with the length of the arc, the strength of the current, and according to whether the light is emitted by the anodic or cathodic portion of the arc. These changeable lines are all more or less diffuse, and this is more particularly the case for the short arc spectrum when a strong current is passed between the poles. This circumstance suggests that the observed displacements are not real, and are attributable to unsymmetrical broadening of the lines, but the author maintains that many of the observed changes in wave-length are greater than can be accounted for on this assumption. Although no explanation of the effects can be given, it is quite improbable that they are of the same nature as the displacements which are observed when the pressure is varied. The view that they are pressure effects would necessitate the assumption of variations of pressure within the arc of such magnitude as to preclude the possibility of this affording a reasonable basis of interpretation.

Similar measurements were also made in the ultra-violet region (λ 2400 to λ 3330), and variations in wave-length with the conditions of the arc discharge of the same kind were found. The results obtained in this region are, however, not nearly so definite as those for the greenish-yellow, and the author considers that it is possible that the apparent displacements may be due to unsymmetrical broadening of the lines. In favour of this view, attention is drawn to the fact that many diffuse lines in the ultra-violet are not displaced at all, whereas all the diffuse lines in the greenish-yellow region are found to undergo a shift of measurable amount.

The fact that all the diffuse iron lines in the greenish-yellow region are variable in wave-length leads to the conclusion that the spectrum of some other element should be employed in the determination of the secondary and tertiary normals in this region. In regard to the region (λ 2400—λ 3330), only certain lines are suitable, and a table is given in which unsuitable lines are indicated.

H. M. D.

Absorption Spectra of Aqueous Solutions of Poly- and Simple Hydrated Salts by Means of a Radiometer. E. J. SCHAEFFER, M. G. PAULUS, and HARRY C. JONES (*Zeitsch. physikal. Chem.*, 1915, **90**, 561—593).—The influence of a number of salts on the intensity of the infra-red absorption bands of water has been carefully studied, and measurements of the intensity of the bands have been made by means of a radiomicrometer used in connexion with a Hilger spectrometer. The salts used were such as possessed no absorption of their own, and included potassium

chloride, sodium chloride, magnesium chloride, magnesium bromide, magnesium sulphate, zinc sulphate, calcium chloride, zinc nitrate, magnesium nitrate, ammonium bromide, and sodium nitrate. The results are expressed by means of a large number of tables and curves. It is shown that non-hydrated salts which have no absorption of their own cause an increase in the intensity of the middle of the water bands. It is suggested that this may be due to a slight shift of the bands toward the red end of the spectrum. Hydrated salts cause a decrease in the absorption of the middle of the water bands. To this observation nitrates form an exception. In general, it can be stated that all aqueous solutions of non-hydrated and non-absorbing salts are more transparent than water for all the wave-lengths made use of in the present investigation ($\lambda = 706$—1426). This is particularly the case for the band $1{\cdot}25\,\mu$. Magnesium nitrate presents a number of irregularities which could be due conceivably to an absorption by the salt. To settle this point, the absorption of magnesium nitrate in both acetone and ethyl alcohol was measured, with the result that this salt is shown to have no absorption at any point. The general result of the work is to show that combined water has a smaller absorptive power than free water, and this is regarded as an additional piece of evidence in favour of the solvate theory.

J. F. S.

Absorption Spectra of a Series of Aniline Dyes and the Separation of Certain Portions of the Spectrum by Means of Gelatin Filters. ADOLF HNATEK (*Zeitsch. wiss. Photochem.*, 1915, **15**, 133—148).—The absorption spectra of some sixty aniline dyes have been examined, and of these twenty-four have been found suitable for use in the preparation of gelatinised filters. The filters are arranged into three groups, for which the range of transmitted light is about 1000 Å, 500—900 Å, and 200—500 Å respectively. In most cases the filters contain a single dye, but in others the absorption is produced by suitable admixture of two or more dyes. Further reduction in the width of the transmitted bands can be obtained by combination of two or more filters.

H. M. D.

Colorations Produced by Some Organic Nitro-compounds, with Special Reference to Tetranitomethane. II. ALEXANDER KILLEN MACBETH (T., 1915, **107**, 1824—1827. Compare T., 1915, **107**, 87).—Some points of interest which arose in the earlier study on the colorations produced by treating tetranitromethane with unsaturated substances are discussed.

In the first place, a rough examination suggested that the depth of colour obtained might be an indication of the relative reactivity or of the amount of residual affinity of a substance. A quantitative spectrographic study of the colours produced by tetrahydro-1:4-thiopyran, 1:4-dithian, and 1:4-thioxan has shown that the reactivities of these compounds are of the same order as Clarke determined in the case of their combination with bromoacetophenone (T., 1912, **101**, 1788).

The existence of inhibitory factors is also revealed. The presense of electronegative atoms (such as Cl) in ethylenic compounds, for example, is one factor, and no colours are obtained also in the case of unsaturated compounds containing conjugated double linkings (ethylene with carbonyl, or nitrogen with carbonyl), except in the aromatic series, which exhibits many anomalies.

The effect of the nature of the solvent medium has also been examined. Light petroleum and chloroform appear to hinder the development of colour, but water accelerates it. It seems that certain solvents have the power of preventing the "nitrite isomerisation" of the tetranitromethane. J. C. W.

Phosphorescence. K. SCHERINGA (*Chem. Weekblad*, 1915, **12**, 1106—1109).—An account of the close relationship between phosphorescence and fluorescence. A. J. W.

The Photo-bromination of Toluene. K. ANDRICH and M. LE BLANC (*Zeitsch. wiss. Photochem.*, 1916, **15**, 148—164, 183—223).—The bromination of toluene has been examined with special reference to the influence of light of varying wave-length on the yield of benzyl bromide. In a preliminary series of experiments, the influence of various solvents on the absorption spectrum of bromine was examined.

The curve of absorption for a solution of bromine in carbon tetrachloride shows a maximum in the blue (400—450 $\mu\mu$), and a minimum in the neighbourhood of $\lambda = 313\ \mu\mu$. Similar selective absorption is also exhibited by solutions of bromine in hexane. On the other hand, the curves for ethyl acetate, benzene, and toluene solutions show gradually increasing absorption with diminishing wave-length. The absorption spectra of solutions in hexane and carbon tetrachloride resemble that of bromine vapour, and the authors draw the conclusion that the bromine in these solutions is largely present in the free condition, whereas in ethyl acetate, benzene, and toluene solutions it is present in the form of complex molecules resulting from the combination of the bromine with the solvent.

Comparative bromination experiments in presence of hexane and ethyl acetate indicate that the free bromine molecules are photosensitive, whereas the solvated molecules are not. This relation affords an explanation of the fact that the photo-sensitiveness of the reaction between bromine and toluene diminishes rapidly as the wave-length of the incident radiation decreases.

The yield of benzyl chloride is found to depend on the presence of oxygen in the reaction mixture, the yield increasing with the amount of oxygen. This has been traced to the oxidation of the hydrogen bromide, whereby bromine is regenerated. Phenolic substances are also formed in these circumstances, and there is some evidence of the formation of intermediate peroxides. Both toluene and hexane, which have been brominated in presence of pure oxygen, exhibit oxidising properties. The yield of benzyl bromide is nearly independent of the wave-length of the incident

light between λ 579 and λ 325 $\mu\mu$; the reaction velocity decreases rapidly below 400 $\mu\mu$, and is not affected by light of wave-length λ 300—λ 202. The addition of water to the reaction mixture reduces the velocity considerably in presence of pure oxygen, but the effect is small in presence of air.

Some convenient light filters and an arrangement for producing spark discharges of high intensity are described. Reference is also made to the action of anhydrous phosphoric acid on potassium bromide as affording a simple method for the production of hydrogen bromide. H. M. D.

Attempts made to Influence the Velocity of Radioactive Transformations by Means of α-Rays. JEAN DANYSZ and LOUIS WERTENSTEIN (*Compt. rend.*, 1915, **161**, 784—787).—The authors have endeavoured to increase the velocity of transformation of uranium-*I* to uranium-*X*, and of mesothorium-*I* to mesothorium-*II*, by means of α-rays, but without success. In the first case, a tube containing, at the commencement, 18 millicuries of emanation was allowed to act for six days on a layer of uranium oxide, U_3O_8, just sufficiently thick to absorb the α-rays. In the second case, an ampoule containing 30 millicuries of emanation was allowed to act for thirteen hours on 3 mg. of mesothorium-radium contained in a capsule covered with mica 0·005 mm. thick. In neither case could the slightest increase in the velocity of transformation be detected, and the authors consider from a calculation of the possible collisions that even the most intimate contacts of the α-rays with the atoms are unable to provoke an artificial radioactivity or a premature transformation of the atom struck.

W. G.

The Charge of Radioactive Recoil. LOUIS WERTENSTEIN (*Compt. rend.*, 1915, **161**, 696—699).—The author has studied the charge of recoil in the case of radium-*D* projected during the transformation of radium-*C*. Measurements were made of the charge received by a cylinder receptor, the source being a deposit of radium-*C*, (1) when the rays had no obstacle to traverse; (2) when they were filtered through a screen of aluminium foil 0·7 μ thick; (3) when they had to traverse a sheet of aluminium foil 0·05 mm. thick, which arrested all the α-rays. The whole apparatus was contained in a vessel having a high vacuum maintained by a Gaede molecular pump giving 0·6 dyne/cm.^{2} as measured on a Knudsen's absolute manometer. All the three measurements were made in one experiment, the screens being moved by an electromagnetic control outside. The difference between the values from (1) and (2) gave the charge of the *a*-rays, and that between (2) and (3) the charge of the α-rays.

In the high vacuum, 0·6 dyne/cm.^{2}, the atoms of radium-*D*, when projected, do not carry an electric charge, but as the pressure rises they acquire a gradually increasing positive charge, which may equal or even exceed that of the α-rays. This positive charge is a consequence of the collisions of the atoms of radium-*D* with the molecules of the surrounding gas, one or more electrons being

separated from the radioactive atom. The pressure under which the recoil attains a charge equal to half of that of the α-rays corresponds with a free path of the atoms projected equal to the distance of the source from the receptor. The experimental results give the value of the mean free path at a pressure of 1 dyne/cm.^{2} as 100 mm., whilst the value calculated from the ionisation produced is 90 mm. The free path of a particle of radium-C calculated in the same way for the initial portion of its path is 440 mm., and the α-rays ionise at their commencement five times better than the α-particles.

At the atmospheric pressure the atoms of recoil behave as univalent ions, and the dissociations of the radioactive atoms resulting from the collisions with the molecules must therefore be followed by recombinations as the velocity of the atoms diminish, this behaviour showing the close analogy existing between the α-rays and the canal rays. W. G.

Influence of Foreign Substances on the Adsorption of Uranium-X_1 by Charcoal. H. Freundlich and H. Kaempfer (*Zeitsch. physikal. Chem.*, 1915, **90**, 681—716).—A large number of experiments have been carried out on the influence of thorium salts and many other substances on the reversal of the adsorption of uranium-X_1 by charcoal. These experiments are in part a repetition of those of Ritzel (A., 1909, ii, 851) and partly an extension of Ritzel's work. It is shown that the presence of small concentrations of thorium salts causes a reversal of the adsorption of uranium-X_1 by charcoal. Thus the presence of 0·0004 millimol. of thorium nitrate increases the amount of uranium-X_1 which remains in solution after shaking with charcoal by about 20%. The action, however, is not specific for thorium or the radio-elements, for a large number of substances, such as zirconium salts, benzoic acid, strychnine nitrate, and basic dyes, have a similar action. A number of points of difference between the action of thorium nitrate and the other substances was noticed. The adsorption of benzoic acid, strychnine nitrate, and zirconium oxychloride was measured by means of the radioactivity of uranium-X_1. The method adopted consisted in determining the end concentration in solutions of these substances of the uranium-X_1 which had been shaken together with these substances and charcoal, and from the amount of reversal of the adsorption of the uranium-X_1 the adsorption of the other substance was deduced. In the case of benzoic acid and zirconium oxychloride, the usual adsorption isotherms were obtained by this method, but in the case of strychnine nitrate there was a tendency to reach a saturation value. In all three cases an end condition was reached which was independent of time. When an attempt was made to determine the adsorption of thorium nitrate by the same method, a difference was noticed in the behaviour from that observed with the other substances in the sense that the end concentration appeared to decrease with time. This decrease could not be confirmed by nephelometric measurements on the oxalate, and was explained by the fact that

a solution of thorium nitrate which has been shaken with charcoal afterwards produces a much smaller reversal of the adsorption of uranium-X_1. This corresponds with the observation of Ritzel, which was confirmed, that freshly produced uranium-X_1 in uranium nitrate solution which has been shaken with charcoal is more strongly adsorbed by charcoal than uranium-X_1 of long standing. The authors explain the above phenomena by the assumption that in thorium and uranyl nitrate solutions small quantities of still undiscovered radio-elements exist, and that these exert a strong reversing action on the adsorption of uranium-X_1, but that they are completely adsorbed by charcoal when shaken with it. Thorium nitrate differs from the other substances which reverse the adsorption of uranium-X_1 in the fact that it not only diminishes the adsorption of uranium-X_1 when it is adsorbed at the same time as the uranium-X_1, but it also causes a reversal of the adsorption if it is added to the charcoal after the uranium-X_1 has been adsorbed. The latter effect is not observed with the other substances. The difference is probably to be explained in the following way: uranium-X_1 is not only concentrated on the surface of the charcoal, but also penetrates into the interior; the same is probably also true for thorium nitrate and the unknown substances mentioned above. These substances can therefore exercise their reversing action on the uranium-X_1 when they are added after it has been adsorbed, whereas the other substances, such as benzoic acid, by adsorption are only concentrated on the surface and cannot therefore exercise this action. The foregoing observations lead to the conclusion that the statement of Soddy (T., 1911, **99**, 72), to the effect that the reversal of the adsorption of uranium-X_1 by thorium is due to the isotropy of the two substances, is not in accordance with experimental facts. On the other hand, the fact that other substances have the same action as thorium does not disprove in any way the isotropy of these two substances. The coefficient of the absorption factor of the adsorption isothermal for both thorium nitrate and uranium-X_1 was found to be very nearly unity. The reversal of the adsorption of uranium-X_1 by other foreign substances does not depend wholly on the adsorption of these substances, and is not purely a decreasing of the power of the charcoal to adsorb uranium-X_1, but rather a hindrance by the foreign substance to the penetration of uranium-X_1 into the interior of the charcoal, much in the same way that adsorbed substances hinder the crystallisation of supersaturated solutions. Ritzel (*loc. cit.*) found that thorium emanation also caused a reversal of the adsorption of uranium-X_1; this the authors find does not occur if the emanation is filtered through wool before it is led into the solution. The reversal observed by Ritzel is therefore to be attributed to dust of thorium nitrate carried over by the emanation. J. F. S.

Transmutation of Chemical Elements. II. W. P. JORISSEN and J. A. VOLLGRAFF (*Zeitsch. physikal. Chem.*, 1915, **90**, 557—560. Compare A., 1915, ii, 134).—The authors have sub-

jected bismuth to a stream of cathode rays with the object of ascertaining whether by this action bismuth becomes radioactive or is converted into thallium. The experiments show that bismuth which has been treated in this way has no action on the leaves of a charged electroscope and has also no action on a photographic plate. On testing the metal for thallium, it is shown that in the untreated metal there is a small quantity of thallium which, although not sufficient to give the usual microchemical reactions, can be detected spectroscopically. The amount of thallium is not increased by the treatment with cathode rays.

J. F. S.

Dielectric Constants of Some Compounds of Vanadium. ALBERT G. LOOMIS and HERMAN SCHLUNDT (*J. Physical Chem.*, 1915, **19**, 734—738).—The dielectric constants of vanadium oxychloride, vanadium oxybromide, and vanadium tetrachloride have been determined by the Drude-Schmidt method at a series of temperatures. The compounds examined were prepared by the Roscoe methods, and full details of the preparation are given in the paper. The following values were obtained for the dielectric constant: vanadium oxychloride, 3·42 at 21°, 3·38 at −70°; vanadium oxybromide, 3·62 at 25°, 3·93 at −2°, and 4·38 at −70°; vanadium tetrachloride, 3·05 at 25°. J. F. S.

Electrical Conductivity and Luminosity of Flames Containing Salt Vapours. H. A. WILSON (*Phil. Trans.*, 1915, [*A*], **216**, 63—90).—The author has studied the influence of an electric field on the velocity of positive ions of salt vapours in flames, together with the relationship of electric conductivity of flames containing salt vapours to their luminosity. Further experiments have been made to show the variation of the conductivity with the concentration of the salt vapour and to determine the relative conductivity due to salts of different metals. From the experimental results it is shown that the luminous vapours of salts in a Bunsen flame are not deflected appreciably by an electric field, and that the positive ions present in the luminous vapour can be made to move out of it by an electric field. The positive ions are not luminous, but can form luminous vapour after recombination. The velocity of the positive salt ions in flames is about 1 cm. per second for 1 volt per cm., and is the same for all salts. The conductivity and luminosity of sodium chloride both vary nearly as the square root of the concentration of the salt vapour in the flame. The conductivities and luminosities of chemically equivalent amounts of sodium chloride and sodium carbonate are equal. A considerable excess of hydrogen chloride does not change the luminosity due to sodium chloride, but it slightly increases the conductivity of the flame. A large excess of hydrogen chloride, obtained by the introduction of chloroform vapour, diminishes the luminosity due to sodium chloride by about 50%, and diminishes the conductivity about six times. The percentage changes in the luminosity and conductivity are independent of the concentration

of the sodium chloride vapour. The chloroform increases the current due to large potential differences, but diminishes the conductivity as measured by the ratio of the current to the uniform potential gradient in the flame. When the drop of potential at the negative electrode is got rid of by placing potassium carbonate on it, the chloroform diminishes the current to about the same extent as the conductivity. The presence of a large amount of potassium carbonate does not change the luminosity due to sodium carbonate, although the potassium carbonate greatly increases the total conductivity. The variation of the conductivity (c) with the concentration (k) for alkali salts can be represented by the equation $k10^4 = (c^2 - 1)/c.(b + ac)$, using proper values for the constants a and b for each salt. This expression can be deduced from the ionic theory, and the fraction of the salt molecules which are ionised is equal to $b/(b + ac)$. Alkali chlorides and carbonates impart equal conductivities to the flame for chemically equivalent concentrations. The percentage of the salt which is ionised when the concentration is small has the following values: cæsium salts, 91%; rubidium salts, 69%; potassium salts, 58%; and sodium salts, 1·6%. The constant b is proportional to the molecular weight of the salt, and according to the theory this shows that all salts give negative ions having the same velocity due to an electric field. The conductivity due to solutions containing a mixture of salts agrees with that to be expected on the ionic theory. J. F. S.

The Influence of Some Hydroxy-acids on the Electrical Conductivity of Boric Acid. J. Böeseken [with R. de Brauw, S. de Waard, and C. van Loon] (*Rec. trav. chim.*, 1915, **35**, 211—224. Compare A., 1915, ii, 136, 667).—Measurements were made of the electrical conductivity of boric acid solutions containing varying molecular proportions of β-hydroxybutyric acid, α-hydroxy*iso*butyric acid, benzilic acid, and α-hydroxydiphenylene-acetic acid. The three last named all give a marked increase in the conductivity, the results showing that the amount of the increase is not directly connected with the dissociation constant of the acid. Apparently the group adjacent to the α-hydroxy-group is of much greater importance in this connexion. With β-hydroxybutyric acid there was a marked diminution in the conductivity, the difference being, however, less than in the case of the other three acids. W. G.

Conductivity and Dissociation of Some rather Unusual Salts in Aqueous Solution. Charles Watkins and Harry C. Jones (*J. Amer. Chem. Soc.*, 1915, **37**, 2626—2636).—The electrical conductivities of solutions of sodium bromate, thiocyanate, thiosulphate, dithionate, pyrophosphate, tungstate, formate, chromate, dichromate, dihydrogen phosphate and phosphate, ammonium iodate, thiocyanate, chromate and dihydrogen phosphate, rubidium iodide, lithium chromate, and potassium ferricyanide have been measured at various concentrations and at 0°, 15°, 25°, and 35°. From these data, temperature-coefficients are

calculated, and the influence of temperature on the ionisation is discussed. H. M. D.

Electrical Conductivity of Certain Salts in Pyridine. EDWARD X. ANDERSON (*J. Physical Chem.*, 1915, **19**, 753—789).—The electrical conductivity of pyridine solutions of silver nitrate, lithium chloride, bromide, and iodide, sodium iodide, potassium thiocyanate, ammonium thiocyanate, mercuric chloride, bromide, and iodide, copper chloride and nitrate, cadmium nitrate, cobalt chloride, and lead chloride have been determined at 0°, 25°, and 50° for a series of concentrations in each case. These substances constitute two series of electrolytes, the one consisting of salts the equivalent conductivity of which increases with increasing dilution, and the other consisting of salts the conductivity of which drops to a minimum. The temperature-coefficients have been calculated, and it is shown that the coefficients between 0° and 25° are larger than those between 25° and 50°. Solutions of lithium bromide, sodium iodide, cobalt chloride, and cadmium nitrate have negative temperature-coefficients. Explanations are given for the minimum conductivity and for the differences in the temperature-coefficients. It has been shown that the anomalous behaviour in equivalent conductivity is due entirely to the presence and properties of the ionisable polymerised solute which predominates in concentrated solutions. J. F. S.

The Conductivity and Viscosity of Solutions in Formamide. P. B. DAVIS, W. S. PUTNAM, and HARRY C. JONES (*J. Franklin Inst.*, 1915, **180**, 567—601).—In a further investigation of the properties of non-aqueous solutions of electrolytes, measurements have been made of the electric conductivity and viscosity at 15°, 25°, and 35° of salts dissolved in formamide. By repeated distillation of formamide, dried over anhydrous sodium sulphate, under reduced pressure in a current of dry air, the conductivity of the solvent has been reduced to a very much smaller value than that previously recorded by Walden (compare A., 1912, ii, 26). The lowest value observed was $K = 2{\cdot}8 \times 10^{-6}$ mho. at 25°.

The salts for which data are recorded are sodium bromide, iodide and chromate, potassium chloride, iodide and thiocyanate, ammonium bromide and iodide, tetramethylammonium chloride and iodide, rubidium chloride, bromide, iodide and nitrate, cæsium chloride and nitrate, lithium nitrate, barium chloride, mercuric chloride, and cobalt bromide.

The results afford further support for the view that the ionising power of a solvent increases with the dielectric constant and the association factor. Salts which form hydrates in aqueous solution afford evidence of combination with formamide. The solutions of these solvated salts show a larger percentage change in conductivity with change in temperature as compared with solutions of non-solvated salts. The percentage temperature-coefficient is found to be approximately proportional to the viscosity of the solutions.

Formamide is the only solvent for which the viscosity of the

solutions examined is less than that of the pure solvent. This is supposed to be connected with the large value of the association factor.

Mercuric chloride is ionised to a greater extent in formamide than in water. H. M. D.

Hydrates of Alcohols and Fatty Acids. Ballistic Electric Investigations. [MISS] JOHANNE CHRISTIANSEN (*Zeitsch. physikal. Chem.*, 1915, **90**, 628—640).—Christiansen has shown (*Ann. Physik*, 1913, [iv], **40**, 107) that when aqueous solutions of salts to which small quantities of non-electrolytes, such as alcohol, have been added are sprayed against a plate they give up considerable quantities of electricity. This electricity is termed *ballo-electricity*. The present paper deals with the potential of the electricity given up when solutions of calcium chloride or sodium chloride in water containing varying quantities of alcohols or fatty acids are sprayed against a platinum plate connected to a sensitive quadrant electrometer. Measurements were made with methyl alcohol, ethyl alcohol, propyl alcohol, butyl alcohol, and amyl alcohol, formic acid, acetic acid, propionic acid, and butyric acid. In the case of all the substances examined it is shown that the voltage at first increases to a maximum, and then falls again to zero with increase in the percentage of the non-electrolyte added. The voltage then changes sign and slowly increases numerically. The point of zero voltage is termed the ballo-electric neutral point. In the case of the first three alcohols, the mixtures at which this point is reached are 1 mol. of methyl alcohol to 1·95 mols. of water, 1 mol. of ethyl alcohol to 3·98 mols. of water, and 1 mol. of propyl alcohol to 8·38 mols. of water, that is, the number of molecules of water have approximately the relationship $2:2^2:2^3$. In the case of the acids, the ratio of the number of molecules of water is $3:3^2:3^3$, etc., for the ascending members of the series. The action is held to be due to a mechanical separation of neutral molecules into ions.

J. F. S.

A Hydrogen Electrode Vessel. WM. MANSFIELD CLARK (*J. Biol. Chem.*, 1915, **23**, 475—486).—After a description of a number of vessels which have been used for the determination of hydrogen ion potentials, the author describes a piece of apparatus which is based on the principle of that devised by Hasselbach (A., 1911, ii, 182). The object of the modification is to enable measurements of hydrogen ion concentration to be made in bacterial and other liquids which are undergoing fairly rapid change. The apparatus consists of a length of fairly wide glass tube, to one end of which a small bulb is attached which is fitted with a neck at the top to take the platinum electrode, and with a three-way tap immediately below the neck for the purpose of connecting with the calomel electrode. The other end of the tube is fitted with a three-way tap, which is connected to a small reservoir containing the liquid under examination and to a hydrogen generator. The

apparatus is used as follows: the apparatus, containing only the platinum electrode, is filled with hydrogen, and then the solution is added until it is about one-third full. Then the apparatus, which is mounted on a rocker, is rapidly rocked for five to ten minutes, so that the electrode is alternately exposed to the gas and immersed in the solution. The measurement is then made, and is found to be at once constant to about 1 millivolt. In many cases a much more constant result is obtained. A series of measurements with milk, gelatin cultures, meat infusion, and peptone solution are given to illustrate the type and constancy of the results.

J. F. S.

The Anodic Solution of Lead. NORMAN MURRAY BELL (*Trans. Faraday Soc.*, 1915, **11**, 79—90).—Experiments have been made to test the supposition that univalent lead ions exist in aqueous solutions (Denham and Allmand, T., 1908, **93**, 424). The anodic solution of lead is determined by measurements in solutions of lead acetate, sodium acetate, potassium hydrogen tartrate, hydrofluosilicic acid, potassium bromide, and sodium thiosulphate at various current densities. Bars of cleaned "pure" lead are used. The loss of weight of the anode is generally greater than is indicated for bivalent ions. With the above solutions, except the two sodium salts, the loss is shown to be due to mechanical and chemical removal of lead, but sodium acetate and thiosulphate give results which appear to indicate the formation of univalent lead ions to the extent of 2·8% and 5·6% respectively. The chemical character of the black deposit formed on lead anodes in thiosulphate solutions has not been determined. C. H. D.

Electrical Transference in Amalgams. GILBERT N. LEWIS, ELLIOT Q. ADAMS, and EDITH H. LAMMAN (*J. Amer. Chem. Soc.*, 1915, **37**, 2656—2662).—When sodium is dissolved in liquid ammonia, a conducting solution is obtained, and according to Kraus the carriers of positive electricity in this solution are the sodium ions, whilst the negative carriers are free electrons. In the expectation that a solution of a strongly electro-positive metal in mercury would show similar behaviour on the passage of a current, experiments have been made to determine the effect of the current on dilute sodium and potassium amalgams.

Sodium and potassium amalgams, prepared by electrolysis, were subjected to the action of a current of from four to eight amperes for several days under conditions which eliminated as far as possible the effect of convection, and the alkali in the anode and cathode compartments was then estimated. The results of these experiments show that the passage of the current through the amalgam was accompanied by the transfer of alkali metal from the cathode to the anode. The number of equivalents transferred per faraday was found to be $2·9 \times 10^{-6}$ in a sodium amalgam containing 3·24 atoms per cent. of sodium and $0·29 \times 10^{-6}$ in an amalgam containing 0·57 atom per cent. In a potassium amalgam contain-

ing 2·16 atoms per cent. of the alkali metal, the transfer per faraday was $3 \cdot 6 \times 10^{-6}$ equivalent.

The diminution in the electrical conductivity resulting from the addition of the alkali metal is attributed to a diminution in the average mobility of the electrons. If the atoms of sodium are supposed to form nuclei of large aggregates of mercury atoms, which aggregates are less easily penetrated by the electrons than are free mercury atoms, the negative transfer of the sodium can be explained. The fact that potassium has a greater transference number is on this view consistent with the fact that potassium produces a greater lowering of the conductivity of mercury as compared with that produced by an equivalent quantity of sodium.

H. M. D.

Application of the Theory of Allotropy to Electromotive Equilibria. II. Passivity of Iron. A. Smits and A. H. W. Aten (*Zeitsch. physikal. Chem.*, 1915, **90**, 723—743).—A theoretical paper in which anodic polarisation and the passivity of iron as brought about either by chemical means or by anodic polarisation are discussed. A number of theories are discussed, and it is shown that the primary manifestation of passivity, which consists in the fact that at moderately low current densities the potential difference between iron and electrolyte increases so that the liberation potential of oxygen is rapidly reached, is not in accord with the oxide theory and cannot be explained by this theory. The charging of iron with oxygen and the resulting oxide formation are secondary manifestations of passivity. It is emphasised that passivity has its situation on the surface of the metal, and it is shown that the appearance of passivity due to all causes, the change from the passive form to the active form, and abnormal cathodic polarisation can all be explained from a common point of view on the basis of the theory of allotropy. Polarisation occurs, not because the heterogeneous equilibrium between the metal and the solution is set up too slowly, but because the metal is compelled to dissolve more rapidly than the inner equilibrium is able to set itself up, whereby the metal surface becomes more noble. A strong experimental confirmation of the new method of consideration is found in the results of Finkelstein (A., 1902, ii, 81), who showed that iron in a solution of ferric sulphate has a more positive potential than iron in a solution of ferrous sulphate of the same concentration. The formula $\Delta = -RT/nF \log_e K/C$ is not obeyed and the formula $\Delta = -RT/F \log_e (K \,.\, C'''/C'')$ may not be applied, because iron in a solution which contains ferric ions cannot be in equilibrium and cannot act as non-soluble electrode. The iron is strongly attacked by such a solution, and the above-mentioned phenomena are the result of a disturbance of the internal equilibrium of the metal surface. It is also shown that the activation curve points to a discontinuity in the mixture series of the pseudo-components. The abnormal cathodic polarisation and the connexion between the allotropy of iron and its passivity are discussed in connexion with the theory of allotropy. J. F. S.

The Thermomagnetic Properties of Various Compounds and the Weiss Theory of Magnetons. KÔTARÔ HONDA and TORAJIRÔ ISHIWARA (*Sci. Rep. Tohoku Imp. Univ.*, 1915, [ii], **4**, 215—260). —The experiments of Ishiwara at low temperatures (A., 1915, ii, 141) have now been extended to higher temperatures. The susceptibility of paramagnetic compounds is not derivable from that of their components by the additive law. Curie's law is only applicable to a very limited number of compounds, but a hyperbolic law, such as that given by K. Onnes and Perrier, is generally applicable over the whole range of temperature within which the same phase is present. Either an abrupt departure from this law or a gradual one extending over a range of temperature indicates a phase change. The susceptibility of all the diamagnetic substances examined is constant for all temperatures within the range of existence of a single phase. The effect of water of crystallisation is different in different compounds. Phase changes are readily detected by means of thermomagnetic observations.

Weiss's theory of magnetons is criticised, the evidence on which it is based being considered insufficient, and the magnetic moments of elements and compounds are calculated from the data in this paper and this vol., ii, 105, leading to the conclusion that the oxygen atom has a greater magnetic moment than that of iron, whilst molecules of the compounds of iron, nickel, and cobalt have magnetic moments which are far greater than those of the ferromagnetic elements themselves. C. H. D.

An Electromagnetic Vacuum Balance. JOHN S. ANDERSON (*Trans. Faraday Soc.*, 1915, **11**, 69—75).—The balance is intended for repeated weighings of silica gels and similar substances without removing from the vacuum. One of the scale-pans of a balance is replaced by a coil of wire with its axis vertical. This moves between two larger coils concentric with it, so connected that the movable coil may be attracted or repelled. The force is varied by varying the current. The balance is enclosed in a bell-jar, which may be evacuated. The beam is released and fixed magnetically by means of an iron core and two solenoids. An electrical arrangement with slide resistances allows the current passing through the weighing coils to be measured. This is calibrated by means of known weights. C. H. D.

Relation between the Thermal Conductivity and the Viscosity of Gases with Reference to Molecular Complexity. J. A. POLLOCK (*J. Roy. Soc. New South Wales*, 1915, **49**, 249—252).—The relation between the thermal conductivity k, the viscosity η, and the specific heat c_v of a gas is expressed by the equation $k=f\eta c_v$, in which the coefficient f has the same value for gases which contain the same number of atoms in the molecule. By the use of Eucken's data (A., 1913, ii, 474) it is shown that the connexion between f and the specific heat ratio $\gamma=c_p/c_v$ may be written in the form $f=7{\cdot}32(\gamma-1)/\gamma^{1{\cdot}3}$. It is also shown that $m\gamma k/\eta$ is approximately constant, m denoting the molecular weight of the gas. H. M. D.

The Thermal Conductivity of Neon. ERICH BANNAWITZ (*Ann. Physik*, 1915, [iv], **48**, 577—592).—From observations made according to Schleiermacher's method, the thermal conductivity of neon at 0° has been found to be $k_0 = 0·0001091$ gr./cal. sec./cm. The temperature-coefficient of the thermal conductivity is 0·00259, which agrees closely with the values for air (0·00253) and argon (0·00260), but is smaller than the value for helium (0·00318).

According to Chapman (*Phil. Trans.*, 1911, [*A*], **211**, 433), the thermal conductivity k, the coefficient of viscosity η, and the specific heat at constant volume c_v are, in the case of monatomic gases, connected by the equation $k/\eta . c_v = 2·5$. By substituting in this equation the values $\eta = 3·036 \times 10^{-4}$ (at 10·1°), $c_v = 0·1474$, $k = 0·00011195$ (at 10·1°), the value of $k/\eta c_v$ is found to be 2·501.

H. M. D.

Determination of the Velocity of Sound and of the Ratio of the Specific Heats of Gases by the Method of Kundt's Dust Figures. GUSTAV SCHWEIKERT (*Ann. Physik*, 1915, [iv], **48**, 593—667).—Measurements have been made of the velocity of sound in various gases at the ordinary temperature, using Kundt's method in combination with tubes of varying diameter and notes of different pitch. Data are recorded for air, nitrogen, oxygen, hydrogen, carbon monoxide, hydrogen chloride, carbon dioxide, nitrous oxide, sulphur dioxide, ammonia, ethylene, and acetylene.

The data are applied to the derivation of the specific heat ratio $k = c_p/c_v$ and of the molecular heats. The following recorded values of the molecular heats at constant pressure c_p at 20° show that for diatomic, and still more for triatomic, gases the molecular heat increases with the density: carbon monoxide, 6·900; nitrogen, 6·905; oxygen, 6·924; hydrogen chloride, 7·046; carbon dioxide, 8·904; nitrous oxide, 9·214; sulphur dioxide, 10·059; ammonia, 8·933; ethylene, 9·773; acetylene, 9·783. These values are compared with the results obtained in direct measurements of the specific heats of the various gases.

H. M. D.

The Specific Heat of Platinum and of Diamond at High Temperatures. A. MAGNUS (*Ann. Physik*, 1916, [iv], **48**, 983—1004).—By means of a modified form of the calorimeter described in a previous paper (A., 1913, ii, 103), measurements have been made of the specific heat of platinum and its variation with temperatures up to about 900°. The heat (Q) liberated by 1 gram of platinum in cooling from $t°$ to $t_0°$ can be expressed by the equation $Q = 0·031590(t - t_0) + 0·0^5 29234(t^2 - t_0^2)$, and from this the specific heat at any temperature t is given by $c_p = 0·031590 + 0·0^5 58468t$.

In Weber's well-known measurements of the specific heat of diamond and graphite at high temperatures, the temperature of the heated substance was determined indirectly by measuring the heat liberated by platinum which had been heated to the same temperature. In view of the greater accuracy of the new measurements of the specific heat of platinum, Weber's data have been

made use of in a recalculation of the specific heat of diamond and of graphite. For diamond $c_p = 0{\cdot}31456 + 0{\cdot}0^3 3824(t - 282) - 0{\cdot}0^6 3168(t - 282)^2$ and for graphite $c_p = 0{\cdot}28815 + 0{\cdot}0^3 46348(t - 225{\cdot}3) - 0{\cdot}0^6 3642(t - 225{\cdot}3)^2$. The equation for the specific heat of diamond is in very good agreement with Weber's data over the entire range of temperature, but in the case of graphite there are discrepancies at temperatures below 500°. H. M. D.

A New Method for Determining the Specific Heat of Liquids. E. J. HARTUNG (*Trans. Faraday Soc.*, 1915, **11**, 64—68).—The method requires the use of about 60 c.c. of the liquid, and gives a high accuracy. It consists in introducing a known weight of ice, enclosed in a bulb, and noting the fall of temperature produced. A small, cylindrical glass bulb contains 1 to 3 c.c. of water and as large a roll of silver gauze as possible. This bulb is sealed, and will sink in the liquid. A glass tube, 15 cm. long and 4 cm. diameter, contains 100 c.c. of mercury, and is provided with a rubber stopper, holding the thermometer, and having a hole large enough to admit the ice carrier. Dry air may be drawn through the apparatus. The calorimeter is a thin copper cylinder, silvered internally and supported in a Dewar vessel. The mouth is closed by a rubber stopper, through which a thin glass stirrer passes.

After placing 60 c.c. of the liquid in the calorimeter, and the weight having become constant, the ice carrier is secured under the mercury in the freezing tube and dry air is drawn through to prevent condensation of water. The tube is cooled to $-5°$, and kept at about $-1°$ after freezing has taken place. The temperature being noted, the bulb is introduced into the calorimeter, which is stirred until the temperature reaches a minimum. The usual corrections are made. The values obtained for mixtures of sulphuric acid and water are in good agreement with those of Thomsen. C. H. D.

A Simple Method of Obtaining Melting Points of Fats, etc. ARTHUR W. KNAPP (*J. Soc. Chem. Ind.*, 1915, **34**, 1121—1122).—Very thin shavings of the fat, wax, or fatty acid are spread over about one half of the bulb of a thermometer, which is fixed in a corked test-tube immersed in a transparent bath. It is easy to determine when the sharp edges of the scrapings soften and when the substance is quite transparent. For crystalline compounds, the bulb of the thermometer may be rolled in the powdered substance, when sufficient will adhere. J. C. W.

The Freezing Point of Benzene as a Fixed Point in Thermometry. JULIUS MEYER (*Zeitsch. physikal. Chem.*, 1915, **90**, 721—722).—Richards and Shipley (A., 1914, ii, 765) recommend the use of the freezing point of benzene as a fixed point for calibrating thermometers. The author holds that benzene purified by the method indicated will have an indefinite freezing point on account of the varying amount of air and other gases dissolved in it. He recommends that it would be preferable to use the melting point of pure benzene crystals as a fixed point. J. F. S.

The Solidification Curve of the System Ammonium Nitrate–Lead Nitrate. B. BOGITCH (*Compt. rend.*, 1915, **161**, 790—791).—The author has determined the solidification points of mixtures of ammonium nitrate and lead nitrate containing from 0—55% of lead nitrate. The temperatures at which solidification commenced and finished were determined in each case for the mixtures containing from 33—45·5% of lead nitrate, the differences between these two temperatures for each mixture increasing rapidly with increase in the lead nitrate content. The temperatures of commencement of solidification were plotted, and by extrapolation the temperature at which lead nitrate should melt was found to be 450—470°. The eutectic mixture contained 33% of lead nitrate. W. G.

The Critical Constants of *n*-Butane, *iso*Butane, and Propylene, and their Vapour Pressures at Temperatures Between 0° and 120°. F. M. SEIBERT and G. A. BURRELL (*J. Amer. Chem. Soc.*, 1915, **37**, 2683—2691).—The substances used were carefully purified by fractionation at low temperatures. The vapour pressures recorded were independent of the relative volumes of liquid and vapour, and the critical phenomena were quite normal. The following values are recorded for the critical temperature (θ), critical pressure (π), and the constants a and b calculated from the van der Waals's equation: *n*-butane, $\theta=153·2°$, $\pi=35·67$ atm., $a=0·02883$, $b=0·005470$; *iso*butane, $\theta=133·7°$, $\pi=36·54$ atm., $a=0·02562$, $b=0·005096$; propylene, $\theta=92·6°$, $\pi=45·34$ atm., $a=0·01668$, $b=0·003692$. H. M. D.

The Vapour Pressures of Sulphur Dioxide and Nitrous Oxide at Temperatures Below their Normal Boiling Points. G. A. BURRELL and I. W. ROBERTSON (*J. Amer. Chem. Soc.*, 1915, **37**, 2691—2694).—The observed vapour pressures of liquid sulphur dioxide between $-11°$ and $-64·5°$ can be represented by the equation $\log p=-1448·01/T+8·425$, and the data for solid nitrous oxide between $-90·6°$ and $-144·1°$ by the equation

$$\log p=-1232·2/T+9·579.$$

The Clausius equation gives 6619 cal. for the mean heat of vaporisation of liquid sulphur dioxide and 5632 cal. for the mean heat of sublimation of solid nitrous oxide.

The observations give $-11·0°$ and $-88·7°$ for the normal boiling points of sulphur dioxide and nitrous oxide respectively.

H. M. D.

The Vapour Pressures of Some Saturated Solutions. MALCOLM PERCIVAL APPLEBEY and WILLIAM HUGHES (T., 1915, **107**, 1798—1814).—If P is the osmotic pressure of a solution of concentration c, then, as a general rule, P/c increases with the concentration of the dissolved substance. According to the boiling-point determinations of Berkeley and Applebey (A., 1911, ii, 1062), concentrated solutions of thallous nitrate appear to be exceptional in that the saturated solution gives a value for P/c which is less than that calculated from the gas equation on the assumption that

the salt is non-ionised. In view of this anomaly, measurements have been made of the vapour pressures of saturated solutions of sodium nitrate, sodium sulphate, and thallous nitrate by a static method covering a range of several degrees in the neighbourhood of the respective boiling points.

The temperature-coefficients at 760 mm. derived from the vapour-pressure curves are: sodium nitrate, 21·3 mm. per 1°; sodium sulphate, 29·2 mm.; and thallous nitrate, 22·3 mm. From the experimental data, the osmotic pressures of the saturated solutions have been calculated, and the results shew that for sodium nitrate and sulphate the value of P/c increases continuously with the concentration, whilst for thallium nitrate P/c first increases, reaches a maximum, and then falls continuously. It is supposed that this anomalous behaviour is connected with the association of the dissolved salt. Special experiments showed that the low boiling point of the saturated thallous nitrate solutions is not due to volatility of the salt.

A form of thermostat is described which gives constant temperatures between 100° and 120° within 0·02°. H. M. D.

Vapour Pressure of Liquid Substances at Low Temperatures. C. Drucker, E. Jiméno and W. Kangro (*Zeitsch. physikal. Chem.*, 1915, **90**, 513—552).—The vapour pressure of hexane, ethyl alcohol, ethyl ether, toluene, chloroform, acetone, carbon tetrachloride, and iodobenzene have been determined at temperatures from +15° to −100°. The pressures were measured by either a McLeod manometer or a horizontal modification of the Huygens manometer. In this way, pressures from 40 mm. to 0·001 mm. were measured with an accuracy of 0·001 mm. The experimental results are given in tables and curves, and are shown to be in good agreement with the values previously obtained by Young. Using the vapour-pressure formula of Kirchhoff-Dupre-Rankine with four terms, it is shown that the experimental results may be calculated with accuracy. This is attained when the four coefficients are derived from the curves, and also when one of them is chosen arbitrarily. These constants are consequently to be regarded as empirical, since they may have different values without affecting the final results. This indicates that it is not possible, from the vapour-pressure measurements alone, to deduce the "Chemical Constants" which correspond with temperatures which are not far removed from the absolute zero. To determine these values accurately, it is necessary to know the specific heat and its changes with temperature at these temperatures. J. F. S.

The Vapour Pressure of Concentrated Sugar Solutions. D. Orson Wood (*Trans. Faraday Soc.*, 1915, **11**, 29—50).—New measurements have been made by a direct method, the solutions being prepared in a glass vessel thoroughly freed from grease and provided with taps. Distilled water is freed from air by boiling in a similar vessel and introduced through one of the taps. Water is then removed by evaporation under reduced pressure, and the

last traces of air removed by heating at 100° and pumping. The concentration is then determined by weighing. The bulb in which the measurements are made is sealed on to this apparatus, and is provided with a stirrer consisting of a sealed glass tube containing short, soft iron rods packed in glass wool. This bulb and the first part of the manometer are enclosed in a water-bath.

Experiments with pure water show that the results are slightly too low. Solutions containing 48, 61, and 69% of sucrose have been examined. The heat of dilution, calculated by means of Kirchhoff's equation, is of the right sign and order. When the results are tested by calculating the hydration, Callendar's factor is found to be about 4, whilst the osmotic pressures are of the right order, but diminish with rise of temperature. This may be due to increased association, and the theoretical meaning of the change is discussed. C. H. D.

The Vapour Pressures and Specific Volumes of Binary Mixtures of Volatile with Non-volatile Liquids. F. H. CAMPBELL (*Trans. Faraday Soc.*, 1915, **11**, 91—103).—The vapour pressures of the liquids are determined by measuring the rise of mercury in an open manometer, caused by allowing a mixture of known composition to escape into a space previously filled with hydrogen. Mixtures of oleic acid with either ether or carbon disulphide give vapour-pressure curves which closely approach the diagonal, whilst in the third pair of normal liquids, aniline and ether, the curve has a point of inflection and cuts the diagonal. It is possible that in this case a measurably volatile solvate is formed. The oleic acid–acetone curve, acetone being associated, lies above the diagonal. Sulphuric acid and ether give a curve with a point of inflection, probably due to a compound, $(C_2H_5)_2O,H_2SO_4$, which may combine with a further molecule of ether. Of pairs of associated liquids, glycerol–methyl alcohol gives a curve like that of oleic acid and acetone, whilst the curve of glycerol and water lies below the diagonal. The specific volume curves are also given. Attempts to apply Dolezalek's theory quantitatively fail, even in the simplest cases. C. H. D.

Some Difficulties in Van Laar's Theory of the Vapour Pressures of Binary Mixtures. R. T. LATTEY (*Trans. Faraday Soc.*, 1915, **11**, 118—120).—Van Laar's formula is shown to be inconsistent with the effects of temperature on the vapour pressure of mixtures of partly miscible liquids, and even with the experimental facts when the comparison is made at constant temperature. The data for methyl ethyl ketone and water mixtures are used for the purpose. C. H. D.

Von Babo's Law and Kirchoff's Equation for the Latent Heat of Dilution. ALFRED W. PORTER (*Trans. Farady Soc.*, 1915, **11**, 19—28).—Two thermodynamical derivations of von Babo's law are given, in order to bring out the assumptions on which it is based. An alternative method of finding the internal latent heat

of dilution is also given. The hydration factor *a* used by Callendar is here employed as representing an effect of alteration of volume of the solvent molecules, the volume of a hydrated salt being greater than that of the anhydrous salt. Callendar's interpretation breaks down, unless water be assumed not to be associated. The value for the hydration is the same on either explanation.

C. H. D.

Heat of Neutralisation and the Quantum Theory. ADOLF HEYDWEILLER (*Ann. Physik*, 1915, [iv], **48**, 681—692).—According to the quantum theory, the heat changes associated with chemical reactions ought to bear some definite relation to the changes which occur in the optical properties, for these are determined by the electron frequencies. On the assumption that the chemical changes are due to changes in the frequencies of the valency electrons, the author has calculated the change in frequency characteristic of the formation of a molecule of water from the corresponding $H^{\cdot}$ and OH' ions, (1) from the heat of neutralisation, and (2) from the change in the refractivity due to ionisation. The first method gives $\nu_m - \nu_i = 0{\cdot}2895 \times 10^{15}$(sec.$^{-1}$) and the second $\nu_m - \nu_i = 0{\cdot}292 \times 10^{15}$(sec.$^{-1}$). The agreement is excellent, and is considered to furnish evidence in favour of the correctness of the author's method. H. M. D.

Contradictions between the Real and Calculated Solubility of Certain Sodium Salts. ALBERT COLSON (*Compt. rend.*, 1915, **161**, 787—790. Compare this vol., ii, 15).—By careful experimental work, the author finds that for sodium chloride the value of ρ at 0° is 28 cal., this development of heat being quite opposed to the marked cooling effect found at 10° and above. In consequence of this, sodium chloride should have a maximum solubility at 1°, which is contrary to fact.

Similarly, in the case of sodium carbonate, whether anhydrous or hydrated, its solubility increases steadily from 0° to 38°, and in consequence ρ should be positive in both cases, but it is not. At the mean temperature 18°, the value of ρ for the anhydrous salt is 5500 cal., and for the decahydrate $-13{,}776$ cal.

Thus, then, the ordinary law of solubility does not apply to either of these common salts. W. G.

History of Specific Gravity Determination. HERMANN SCHELENZ (*Chem. Zeit.*, 1915, **39**, 913—915).—A historical description of the methods and apparatus employed for specific gravity determinations from the earliest times to the seventeenth and eighteenth centuries. G. F. M.

A Convenient Thermostat for Accurate Specific Gravity Determinations and a Gas Pressure Regulator. K. C. BROWNING and C. T. SYMONS (*Trans. Faraday Soc.*, 1915, **11**, 60—63).—A large copper tank is used as the thermostat, provided with stirring paddles on a horizontal shaft. The shaft is driven by a chain

from a spindle, driven through a spring coupling attached to an electrically-driven worm reduction gear. The heating is either electrical or by gas. For electrical heating, a heavy platinum wire is fused into the bottom of a Lowry thermo-regulator, where it is in contact with mercury. The other contact is a platinum wire mounted on a thin brass rod, having a fine thread cut on it, a 4-volt accumulator being in series with the mercury thread, the platinum point, and a relay. When contact is made, the relay turns on part of the heating current. By shunting the platinum-mercury contact with a pair of insulated aluminium plates, each about 12 sq. in., immersed in water, the sparking is so far decreased as not to cause fouling of the mercury.

A gas regulator is also described, consisting of a brass cylinder with a horizontal partition carrying the valve seating, the valve stem being connected with a sheet of rubber insertion, to which it is attached by two concave-convex washers. The regulator is set by adjusting the weight on the valve. C. H. D.

The Critical Point of Gases Liquefied with Difficulty: Nitrogen, Carbon Monoxide, Oxygen, Methane. ETTORE CARDOSO (*J. Chim. Phys.*, 1915, **13**, 312—350).—A detailed account of work, part of which has been previously published (compare A., 1915, ii, 411). By measurements of the densities of co-existing liquid and vapour at various temperatures, the critical density of carbon monoxide is found to be 0·3110 and of methane 0·1623. The author considers that the precision with which the critical data are determinable is frequently over-estimated. The errors attaching to the values obtained for the four gases by the author are probably less than $\pm 0·1^{\circ}$ for the critical temperature and $\pm 0·1$ atmosphere for the critical pressure. H. M. D.

An Interpretation of Van der Waals's Equation from the Point of View of Volume Determined by Equilibrium of Pressures. W. V. METCALF (*J. Physical Chem.*, 1915, **19**, 705—719).—A theoretical paper in which, reasoning from the point of view that the volume of a gas or liquid under given conditions is due to an equilibrium of opposing pressures, it is shown that this equilibrium is represented by the van der Waals equation, thus: $p + a/v^2 = RT/(v-b)$. The author names the various pressure quantities, thus: external pressure + cohesive pressure = elastic pressure. From kinetic considerations it is shown that, in the case of a stable liquid, the elastic pressure, which tends to increase the volume, increases with density more rapidly than does the cohesive pressure, which tends to decrease the volume. The difference between the density coefficients of these two pressures decreases as the density of the liquid decreases. The above-mentioned propositions are used to interpret the various parts of the van der Waals curves. Explanations are given for the metastable portions of both the PV and TV curves. J. F. S.

[Compressibilities of the Elements and their Relations to Other Properties]. Correction. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1915, **37**, 2696—2697).—The substitution of more accurate values for the atomic volumes given in the previous paper (A., 1915, ii, 518) does not in any way invalidate the conclusions which were drawn. In nearly every case the effect of the substitution is to improve the agreement between the calculated and observed values. H. M. D.

The Viscosity Coefficients of Mixtures of Helium and Hydrogen. ARTHUR GILLE (*Ann. Physik*, 1915, [iv], **48**, 799—837).—The viscosities of mixtures of hydrogen and helium have been measured at 0°, 15°, and 100° by the transpiration method. Experiments with air, which were made to test the apparatus, gave $\eta=1\cdot8196\times10^{-4}$ at 19·83° whence $\eta=1\cdot7221\times10^{-4}$ at 0°. For helium, the coefficients obtained were $\eta\times10^4=1\cdot8925$ at 0°, 1·9611 at 15°, and 2·3408 at 100°; and for hydrogen, $\eta\times10^4=0\cdot8772$ at 14·79°.

The viscosity coefficients for mixtures are only approximately represented by Puluj's formula; a much closer agreement is found when the results are applied to Thiesen's formula (*Verh. Deutsch. Phys. Ges.*, 1902, **4**, 357).

The influence of temperature on the viscosity of the mixtures is satisfactorily expressed by Sutherland's formula, but there is some evidence that mixtures falling near the middle of the series would begin to deviate from the requirements of this formula at temperatures below 0°. H. M. D.

The Study of the Density and Viscosity of Aqueous Solutions, with Special Reference to Nitric Acid. II. Viscosities. WILLIAM ROBERT BOUSFIELD (T., 1915, **107**, 1781—1797. Compare *ibid.*, 1407; A., 1915, ii, 744).—An improved form of viscometer of the gravity flow type is described, for which it is claimed that an accuracy of 1 in 1000 is readily obtainable. Water is the only liquid which is admissible for the calibration of viscometers which are to be used in the investigation of aqueous solutions, and, contrary to previous statements, the author has found it quite suitable as a calibrating fluid, although it is admitted that small variations in the time of flow do occur for which no explanation can be given. In connexion with the use of water as a calibrating liquid in viscosity work, it has been found that the exponential formulæ given by Thorpe and Rodger to represent the influence of temperature on the viscosity do not represent their experimental results so closely as the formula $\eta=0\cdot010514\{1+0\cdot0251(\theta-18)+0\cdot000115(\theta-18)^2\}^{-1}$.

The viscosities of $N/32$-, $N/16$-, $N/8$-, $N/4$-, $N/2$-, and N-solutions of nitric acid were measured at 4°, 11°, 18°, and 25°. The influence of temperature on the variation of the viscosity with the temperature is shown by a comparison of the values of the equivalent viscosity increment as measured by $(\eta_w-1)/m$, where η_w is the viscosity relative to that of pure water at the same temper-

ature, and m is the number of equivalents of acid per litre. At 4° the recorded values are all negative, at 18° and 25° all positive, whilst at 11° the increment shows a change of sign. By means of curves, it is shown that the several values of the increments lie on smooth curves, the interpretation of which is discussed in terms of the theory that the viscosity of a solution is approximately a simple function of the relative sizes of the different groups of molecules in the solution. In the particular case under investigation, the three groups concerned are the nitric acid molecules, the dihydrol, and the trihydrol molecules, and account is taken of these in the author's interpretation of his observations.

H. M. D.

The Viscosities of Solutions of Cæsium Salts in Mixed Solvents. P. B. DAVIS and HARRY C. JONES (*J. Amer. Chem. Soc.*, 1915, **37**, 2636—2642).—Measurements have been made of the viscosities of solutions of cæsium chloride and cæsium nitrate in binary mixtures of water with methyl alcohol, ethyl alcohol, and acetone at 15°, 25°, and 35°. Similar measurements have already been made for solutions of rubidium and potassium salts. The interest attaching to the salts of these three metals lies in the fact that their atomic volumes are greater than those of all other metals. The atomic volume decreases in the order—cæsium, rubidium, potassium, and any peculiarities shown by solutions of rubidium and potassium salts may therefore be expected to be shown by cæsium salt solutions in greater degree.

Generally speaking, the salts of these three metals are the only ones which lower the viscosity of water. This has been explained by reference to the large volume of the cations, resulting in a reduction of the frictional surface in comparison with that of pure water.

As in the case of rubidium and potassium salts, the transition from negative to positive viscosity, as the proportion of non-aqueous solvent in the mixture increases, is shifted towards the non-aqueous end of the series of mixtures, and this effect is more marked with cæsium than with rubidium.

H. M. D.

Willard Gibbs's Adsorption Coefficient. ALFRED W. PORTER (*Trans. Faraday Soc.*, 1915, **11**, 51—52).—A simple proof of Gibbs's adsorption theorem, obtained by taking the solution in contact with its vapour, and considering a transformation in which an infinitesimal evaporation takes place, so that the vapour pressure, which is better known, takes the place of the osmotic pressure. The formula is extended to the case of strong solutions, for which it still holds good, although the correcting term becomes relatively large.

C. H. D.

A Simple Method of Deriving the Gibbs Adsorption Formula. F. J. HARLOW and R. S. WILLOWS (*Trans. Faraday Soc.*, 1915, **11**, 53—54).—A simple thermodynamical proof of Gibbs's adsorption formula is given, avoiding the use of the chemical potential, and

obtaining the result in terms of osmotic pressure (compare preceding abstract). C. H. D.

Determination of the Coefficient of Diffusion of Potassium Chloride by an Analytical Method. A. GRIFFITHS, J. M. DICKSON, and C. H. GRIFFITHS (*Proc. Physical Soc. London*, 1916, **28**, 73—80).—The diffusometer described consists essentially of a series of parallel vertical tubes, the lower ends of which communicate directly with a reservoir of large capacity containing the salt solution. The greater part of the reservoir is above the lower ends of the diffusion tubes, and by the action of gravity, the concentration of the solution in this region is kept approximately constant. The upper ends of the diffusion tubes open into a small chamber provided with inlet and outlet tubes. Pure water enters through the inlet tube, and the dilute salt solution leaving by the outlet tube is collected and analysed. In carrying out an experiment, time is allowed for the attainment of the steady state. This requires several days, and the complete determination may take six weeks.

The results obtained give 1.703×10^{-5} for the mean value of the diffusivity of potassium chloride at 18·5° in a solution of $3N$ concentration. H. M. D.

Velocity of Diffusion and Hydration in Solution. M. PADOA and FERNANDA CORSINI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 461—467).—By means of an apparatus differing slightly from those employed by previous investigators, the authors have studied the diffusion in aqueous solution of various non-electrolytes with the object of determining their molecular weights, and, consequently, the extent to which they are hydrated (compare Herzog, A., 1911, ii, 23). The measurements were made at constant temperatures, ranging from 20° to 24° in the different cases, and the viscosity constants, ξ, are calculated from Bingham and White's results (A., 1912, ii, 1144). The results obtained are summarised in the following table, k being the diffusion coefficient, and v the specific volume, and the hydration being expressed in mols. of water per mol. of the compound:

	k.	v.	ξ.	Mol. wt. Calc.	Mol. wt. Found.	Hydration.
Methyl alcohol	0·739	1·262	0·009172	32	66·6	1·9
Ethyl alcohol	0·396	1·246	0·01006	46	319·0	15·0
Glycerol	0·555	0·793	0·009172	92	250·0	8·9
Phenol	0·525	0·932	0·009116	94	214·0	6·7
Sucrose	0·442	0·630	0·009616	342	530·0	10·5
Acetamide	0·709	0·870	0·009172	59	109·0	2·8
Hexamethylenetetramine	0·543	0·753	0·009838	140	221·0	4·4

Although these results are slightly incorrect, owing to the fact that the calculated values of v do not apply exactly to the hydrated compounds, a pronounced tendency to undergo hydration is evident.

Padoa and Matteucci (A., 1915, ii, 676) have shown that in

benzene solution aromatic hydrocarbons exhibit no appreciable power of combining with the solvent. This is borne out by the results of measurements of the diffusion of naphthalene, diphenyl, and dibenzyl in benzene solution; the values of the molecular weight found in this way are 121, 152, and 180 respectively, the theoretical values being 128, 154, and 182. T. H. P.

Influence of Glycerol, Dextrose, Alkali Nitrates and Sulphates, and Ammonium Salts on the Solvent Power of Water. JAMES CHARLES PHILIP and ARTHUR BRAMLEY (T., 1915, **107**, 1831—1837).—By the method described in a previous paper (compare A., 1915, ii, 236), experiments have been made to determine the effect produced by the above-mentioned substances on the distribution of ethyl acetate between water and benzene at 20°. For all the dissolved substances examined, excepting ammonium nitrate, the equivalent relative lowering of the solvent power increases as the concentration decreases.

From a comparison of the values of the lowering of the solvent power with those deduced from earlier observations on the influence of dissolved salts on the solubility of hydrogen, oxygen, ethylene, and acetylene in water, it is found that the authors' values are greater except in the case of the nitrates. Since the values are calculated on the assumption that the added substance has no solvent power of its own, it follows that they must be regarded as minimum values. For this reason, the equivalent lowerings yielded by the distribution method are probably nearer the truth, and for the majority of the dissolved substances the specific character of the reference substance is of less significance in the method used by the authors than in other work of the same kind. H. M. D.

The Electrical Synthesis of Colloids. H. T. BEANS and HERBERT E. EASTLACK (*J. Amer. Chem. Soc.*, 1915, **37**, 2667—2683).—The experiments described were made with the object of throwing light on the nature of the electrical method of producing colloidal solutions.

In a preliminary calculation of the conductivity due to colloidal particles of gold, for which the size, charge, and mobility are known, it is shown that the conductivity due to the colloid itself is negligibly small in comparison with the observed conductivities of colloidal gold solutions.

Comparative experiments, in which the increase in the conductivity due to the electrical dispersion of gold and platinum was determined, showed that the average increase for sols of approximately the same depth of colour is about eight times as large for platinum as for gold. The platinum sols were invariably more stable than the gold, remaining apparently unchanged on keeping for several weeks, whilst the gold sols coagulated in from two to twenty-four hours. The greater stability of the platinum sols is probably connected with the presence of small amounts of electrolyte formed by oxidation of the metal during the process of dispersion.

In accordance with this view, it has been found that certain anions have a stabilising influence on red gold sols, and this property may be utilised in the preparation of stable colloidal solutions of the metal. Such anions are chlorine, bromine, iodine, and hydroxyl, and a marked effect is observed in concentrations ranging from 0·00005*N* to 0·005*N*. The stabilising effect is not observed if the gold is dispersed in pure water and the electrolyte added subsequently. The lower limiting anion concentration appears to be independent of the concentration of the colloid formed over a wide range, and the upper limit is to some extent influenced by the coagulating power of the associated cation.

Other anions appear to have no influence on the stability of red gold sols, negative results being obtained with solutions containing small quantities of fluorides, nitrates, chlorates, and sulphates.

In all these solutions the colloidal particles are negatively charged, and the stabilising effect of certain anions would seem to be determined by the ability of these ions to form stable complexes with gold. Attempts to detect gold in the filtrate after coagulation of the sols gave, however, negative results, from which it is inferred that the amount of the gold compound which is necessary to produce a stable colloid is extremely minute.

The above observations lead to the conclusion that the electrical method of colloid synthesis involves a primary thermo-mechanical dispersion of the metals, and the subsequent reaction of the highly disperse metals with certain ions present in the surrounding medium, resulting in the formation of negatively charged colloidal complexes. H. M. D.

Influence of Light on the Stability of Colloidal Solutions. H. Nordenson (*Zeitsch. physikal. Chem.*, 1915, **90**, 603—626).—The influence of light from a quartz mercury lamp on a number of sols has been investigated spectrophotochemically and ultramicroscopically. It is shown that light has a slow, coagulating influence on metal colloids which is very similar to the influence exercised by a weak electrolyte. The quantity of light necessary to bring about a visible coagulation is very large, which in all probability explains the negative results of other investigators. There is no chemical change occasioned in the disperse phase, consequently, so far as this phase is concerned, the change is to be regarded as purely physical. The photo-action does not bring about chemical changes in the dispersion medium, and the action only takes place if the colloid is present, during the action of the light, in the dispersion medium. Various types of rays have an analogous action, which is independent of the charge on the colloidal particles. Thus ultraviolet light and β-rays act on both negative and positive colloids. The action cannot therefore be regarded as due to a photo-electric emission of electrons or to the supply of certain charges by the light rays. In all cases the photo-coagulation is accompanied by a decrease in the total charge of the colloid. This decrease in the total charge may be due to one of the following causes: (i) a change in the dissociation of the adsorbed electro-

lytes; (ii) the setting up of potential differences after the manner of those in the Becquerel effect; and (iii) an adsorption of hydrogen or hydroxyl ions from the dissociated water. In any case, there is a specific photo-chemical action which occasions a disturbance of the adsorption equilibrium on the colloid, and thus effects an increase in the size of the particles. This can then be continued after the removal of the light. J. F. S.

Application of the Idea of Expansibility Tension to the Theoretical Study of Chemical Equilibria. L. GAY (*J. Chim. Phys.*, 1915, **13**, 302—311. Compare A., 1915, ii, 326).—A theoretical paper in which the conception of expansibility tension is applied in the derivation of a general formula for the displacement of the equilibrium in a mixture resulting from a change in the volume, pressure, or temperature. H. M. D.

The Ternary System, Carbon Tetrachloride, Alcohol, and Water. HARRY A. CURTIS and ESBON Y. TITUS (*J. Physical Chem.*, 1915, **19**, 739—752).—A large number of experiments have been carried out to determine the critical solubility data of ternary mixtures of the above three components. Further experiments have been made to establish the relationship between the density, composition, and refractive index of the homogeneous ternary mixtures. From the experimental data, the equilibrium line between the one-liquid phase and the two-liquid phase systems has been located on the composition diagram for the temperature 19·75°. The general shape of the critical solubility surface in the composition-temperature prism has been determined over a range of about 50°. It has been found that this surface rises abruptly from isotherm to isotherm, that is, temperature has but little effect on the mutual solubility of the three components. The index of refraction has been determined for eight series of homogeneous ternary mixtures. It has been found that as water is added to a mixture of carbon tetrachloride and alcohol rich in alcohol, the refractive index at first increases and then decreases. As mixtures richer in carbon tetrachloride are used, the maximum refractive index is reached with less and less water, until finally, with mixtures containing initially more than 35% of carbon tetrachloride, the addition of water causes the refractive index to decrease continually. The densities have been determined for eight series of homogeneous ternary mixtures. It has been found that the addition of water to a carbon tetrachloride–alcohol mixture rich in alcohol increases the density uniformly, whilst the addition of water to a mixture rich in carbon tetrachloride lowers the density. The slope of the density curves does not, however, change sign at the point where the density of the initial mixture is unity, but at a point somewhat higher than this, showing that the volume of the ternary mixture is less than the sum of the volumes of the components. It is shown that the determination of two of the physical properties of a ternary mixture does not always fix its composition. J. F. S.

Equilibria in the Systems of the Higher Alcohols, Water, and Salts. G. B. FRANKFORTER and STERLING TEMPLE (*J. Amer. Chem. Soc.*, 1915, **37**, 2697—2716. Compare Frankforter and Frary, A., 1913, ii, 685).—In extending the earlier investigation (*loc. cit.*), the authors have selected the systems *n*-propyl alcohol–sodium carbonate–water, *iso*propyl alcohol–potassium fluoride–water, *iso*propyl alcohol–potassium carbonate–water, allyl alcohol–potassium fluoride–water, allyl alcohol–potassium carbonate–water, allyl alcohol–sodium carbonate–water, and allyl alcohol–sodium chloride–water. The method of representing such systems by triangular co-ordinates is described, but the results are represented in part by rectangular co-ordinates with the percentage of alcohol in the solvent plotted against the percentage of salt in the solvent.

The *n*-propyl alcohol used was purified by successive dehydration with potassium fluoride, quicklime, magnesium amalgam, sodium amalgam, and again quicklime; it then had b. p. 97·3—97·5°/752 mm., D^{20} 0·8032, n_{H_α} 1·39023, whilst *iso*propyl alcohol purified by successive treatment with potassium fluoride, quicklime, sodium amalgam, and quicklime had b. p. 82·5°, D^{20} 0·7881, $n^{20}_{H_\alpha}$ 1·37960.

Potassium fluoride and potassium carbonate were found to be satisfactory dehydrating agents for the above-mentioned alcohols. No evidence was forthcoming as to any relation between the salting-out effect and the chemical constitution of the salts or of the alcohols, and it would appear that the effect is a function of the solubility of the salt in water and in the alcohol concerned, together with the amount of water with which the salt unites to form its lowest hydrate and with the ability of the alcohol to replace the water of hydration. D. F. T.

Relative Affinity of Metals in Non-aqueous Solutions and their Reactivity in Insulating Media. I. JNANENDRA CHANDRA GHOSH (*J. Physikal. Chem.*, 1915, **19**, 720—733).—The author has studied the action of a number of metals on solutions of salts in a series of non-conducting solvents with the object of ascertaining whether chemical replacements take place in solutions of salts which are not ionised. Solutions of ferric chloride, mercuric chloride, mercuric cyanide, cadmium iodide, and lead oleate in benzene, toluene, nitrobenzene, aniline, chloroform, amyl alcohol, amyl acetate, and ethyl acetate were shaken in sealed glass tubes at 21° with the metals mercury, copper, lead, iron, tin, nickel, zinc, and magnesium. The specific resistance of each solution was measured by the replacement method. In every case the resistance was very high, the value varying between 45×10^{10} and $0·25 \times 10^{6}$ ohms. It is shown that magnesium, zinc, and lead replace iron in ferric chloride in all the solvents used; tin replaces iron in most cases; copper replaces iron in aniline solution, and probably in amyl alcohol solution. Mercury does not replace iron in any solvent, but reduces the ferric chloride to ferrous chloride in all the solvents except aniline, in which case there is no action. Magnesium, zinc, and copper replace mercury in mercuric chloride in all cases. Iron

replaces mercury in mercuric chloride in ethyl acetate, amyl acetate, and amyl alcohol solutions. Lead has no action on mercuric chloride in chloroform solution, but in all other cases it reduces mercuric chloride to mercurous chloride. Copper replaces mercury in mercuric cyanide in all solutions. Iron replaces mercury in nitrobenzene and amyl alcohol solutions, magnesium replaces mercury only in amyl alcohol solution, and lead replaces mercury in the cyanide in amyl alcohol and amyl acetate solutions. In other cases there was no action. Magnesium replaces cadmium in cadmium iodide in all solutions, whereas zinc does not replace it in any; iron replaces cadmium in aniline, chloroform, and amyl alcohol solutions, and copper replaces cadmium in aniline, chloroform, amyl alcohol, and amyl acetate solutions. Magnesium, copper, and zinc replace lead from lead oleate solutions in all the solvents; iron has no action in benzene, chloroform, nitrobenzene, and ethyl acetate solutions of lead oleate, and mercury has no action on any of the solutions of lead oleate. It is thus shown that the replacement series is not at all a characteristic of the replacing metal, but is dependent on the mutual relationship of the metals, the acid radicles, and the solvent present in a given combination. A series of experiments was carried out with solutions of mercuric iodide and mercuric chloride in ethyl ether, ethyl acetate, glycerol, carbon tetrachloride, chloroform, benzene, toluene, and carbon disulphide. These solutions were shaken with silver, and in every case mercury was deposited, thus showing that the order of replacement is the same in all cases as in water.

J. F. S.

Dynamic Researches on the Formation of Some Aromatic Sulphones Under the Influence of Aluminium Chloride in a Medium of Benzenesulphonyl Chloride. S. C. J. OLIVIER (*Rec. trav. chim.*, 1915, **35**, 166—179. Compare A., 1914, i, 676, 818; ii, 846).—The author has determined the velocity of formation of sulphones from benzene and chlorobenzene on adding them to a solution of aluminium chloride in benzenesulphonyl chloride at 30°. The velocity constant, *K*, was calculated, assuming that the compound, $C_6H_5\cdot SO_2Cl,AlCl_3$, reacts with the benzene or chlorobenzene, the solvent not being able to remove any of the aluminium chloride from its combination. The results show that one molecule of aluminium chloride cannot transform more than one molecule of benzenesulphonyl chloride, and that for low concentrations of aluminium chloride the values of *K* tend to decrease during the reaction. At high concentrations the formation of sulphone is a true bimolecular reaction. An increase in the concentration of the aluminium chloride or of the chlorobenzene causes a diminution in the value of *K*.

The molecular weight of the combination $C_6H_5\cdot SO_2Cl,AlCl_3$ in solution in benzenesulphonyl chloride was determined by cryoscopic methods, and gave no indication of association with increase in concentration of the aluminium chloride. On combinations of sulphones with aluminium chloride, the above solvent exerts a

greater or less dissociating action. The results show that for the same solvent the relative velocities of introduction of a second substituent are shown by $C_6H_6 > C_6H_5Cl$. W. G.

Determination of Ionisation Constants and the Titration of Weak Bases by the Conductivity Method. CH. DE ROHDEN (*J. Chim. Phys.*, 1915, **13**, 261—301).—The methods usually employed in the determination of the ionisation constants of weak acids and bases depend on the measurement of the degree of hydrolysis of their salts in aqueous solution. The equilibrium relations in solutions of such salts are discussed, and attention is drawn to the essential difference between the hydrolysis constants (1) when the acid and base are both weak, and (2) when the acid is strong and the base weak, or vice versâ. The difference gives rise to little ambiguity so long as the salt falls into one or other of these limiting groups, but the hydrolysis constant of a salt which occupies an intermediate position is a quantity which cannot be defined by either of the ordinary formulæ. The magnitude of the hydrolysis constant is determined by the ionisation constants of the acid, base, and water, and on this account hydrolysis constants are not of primary significance.

A detailed description is given of a method for the determination of the ionisation constants of weak bases from measurements of the electrical conductivity of solutions after the addition of successive quantities of a standard solution of hydrochloric acid. This addition was effected without any appreciable change in the volume of the solution.

The results obtained for aniline and for *o*-, *m*-, and *p*-chloroaniline are recorded. H. M. D.

Reaction Velocity in a Viscous (Heterogeneous) Medium. RAPHAEL H. CALLOW (*Trans. Faraday Soc.*, 1915, **11**, 55—59).—The effect of the presence of gelatin on the velocity of hydrolysis of methyl acetate has been determined. Results cannot be obtained with sodium hydroxide, on account of its reaction with the gelatin, but with hydrochloric acid the change in the velocity constant is small in comparison with that of the viscosity, being only 10% below the normal, even in the case of a jelly which is completely set. The form of the relation between viscosity and velocity has not been fully determined. C. H. D.

Aspirin. III. Anomalies of the Decomposition of Aspirin by Water. D. E. TSAKALOTOS and S. HORSCH (*Bull. Soc. chim.*, 1915, [iv], **17**, 401—406. Compare A., 1915, ii, 47, 433).—A quantitative study of the decomposition of aspirin in aqueous solution at 23°, 50°, and 60°, the rate of decomposition being measured by removing 25 c.c. of the solution at given intervals and titrating this against *N*/50-barium hydroxide. At 50° the reaction was also followed by electrical conductivity measurements. In each case the velocity curve shows two minima, the times at which these occur varying with the temperature. W. G.

The Indirect Determination of Velocity of Hydrolysis by the Polarimetric Method. JAMES CODRINGTON CROCKER (T., 1915, **107**, 1762—1765).—A mixture of sucrose, formamide, and hydrochloric acid was made up, and the change in the rotation of the solution at constant temperature followed in the polarimeter. The acid hydrolyses the formamide and is partly used up in the process. It also hydrolyses the sucrose, remaining unchanged in amount by this reaction. The rate of hydrolysis of the sucrose, being dependent on the amount of acid present, gradually diminishes in proportion as the formamide is decomposed. From the rate at which the velocity of inversion of the sucrose decreases, the velocity of hydrolysis of the formamide can be arrived at. For the method of calculation, the original must be consulted. The rotation of the sucrose solution is not appreciably affected by formamide. Data are given showing that a satisfactory value for the velocity constant for the hydrolysis of formamide can be obtained by this method, the principle of the method being applicable to any reaction during which the hydrolyst changes in concentration, and at the same time can act as a simple catalyst on a third substance present in the solution. T. S. PA.

Velocity of Crystallisation of Supersaturated Solutions. ERNESTO CABALLERO Y LÓPEZ (*Anal. Fis. Quim.*, 1915, **13**, 350—375).—An investigation of the effect of mechanical, physical, physico-chemical, and chemical influences on the velocity of crystallisation of supersaturated solutions of the sulphates of sodium, potassium, copper, zinc, ferrous iron, magnesium, and potassium aluminium. A. J. W.

The Catalytic Hardening of Fats by Means of Nickel Oxides. W. MEIGEN (*J. pr. Chem.*, 1916, [ii], **92**, 390—411. Compare Meigen and Bartels, A., 1914, i, 482).—In reply to Bedford and Erdmann (A., 1913, i, 701) and Siegmund and Suida (A., 1915, ii, 626), the author submits the evidence as to the activity of an unisolated nickel suboxide during the catalytic reduction of fats, to a critical survey, and confirms the opinion already expressed by Meigen and Bartels (*loc. cit.*; Normann and Pungs, A., 1915, ii, 159; Bosshard and Fischli, A., 1915, ii, 788) that oxides of nickel exhibit activity as catalysts only when they contain a certain amount of the free metal. Further experimental evidence with other oils is adduced in support of this view, and stress is laid on the untrustworthiness of specific gravity or electrical conductivity data as evidence of the composition of the catalyst after a reduction experiment. Such results must be dependent on the nature and amount of the organic impurities included in the finely divided nickel, and these, indeed, also can affect the sensitiveness of the carbon monoxide test for the presence of free nickel. The free nickel can be removed fairly satisfactorily from a used nickel oxide catalyst by a magnet, and in this way the author obtained fractions which contained more nickel than could be present even in

a suboxide of the formula Ni_3O, so that the presence of free nickel can scarcely be denied.

From the facts that metallic nickel is known to be an effective accelerator and that it can be found in nickel oxide which has been used as a catalyst, the author is unable to accept the suggestion that nickel oxide owes its apparent catalytic activity to the formation of a suboxide, the presence of which is not proved and the catalytic properties of which are merely postulated. D. F. T.

[Determination of] Molecular Weights of Gases by an Evaporation Method. H. L. TRUMBULL (*J. Amer. Chem. Soc.*, 1915, **37**, 2662—2667).—Measurements have been made of the rate at which water evaporates in contact with dry air, carbon dioxide, and hydrogen at atmospheric pressure. The entire apparatus was immersed in a thermostat maintained at constant temperature ($25·07° \pm 0·01°$). The rate of evaporation (dw/dt) multiplied by the barometric pressure (B) is constant for a given gas. The values of $B.dw/dt$ for the three gases are approximately in the inverse ratio of the square roots of the densities of the gases, indicating that the rate of vaporisation is determined by the rate of diffusion.
H. M. D.

The Valency Theory of J. Stark from a Chemical Point of View. DOROTHY A. HAHN and MARY E. HOLMES (*J. Amer. Chem. Soc.*, 1915, **37**, 2611—2626).—An account is given of Stark's electron theory of valency in its application to the interpretation of chemical phenomena. The account represents an abstract of a treatise by P. Ruggli ("Die Valenzhypothese von J. Stark von Chemischen Standpunkt," Stuttgart, 1912). H. M. D.

An Improved Form of Gas-washing Bottle. F. R. VON BICHOWSKY and H. STORCH (*J. Amer. Chem. Soc.*, 1915, **37**, 2695—2696).—In its simplest form, the apparatus consists of an ordinary wash-bottle, which in operation is laid on its side. The tube, which reaches to the bottom of the bottle, is slightly constricted below the cork and given a very slight inclination to the horizontal. The gas to be washed enters the bottle through this tube and forms bubbles at the constriction, opposite to which and on the lower side of the tube is a sufficiently wide aperture to admit freely the entrance of the liquid in the bottle. H. M. D.

An Automatic Vacuum Pump. OTTO MAASS (*J. Amer. Chem. Soc.*, 1915, **37**, 2654—2656).—A form of Töpler pump which works automatically in conjunction with an aspirator. No mechanical spring or valve is involved, and experience has shown that it can be allowed to run with perfect safety for an indefinite period.
H. M. D.

Inorganic Chemistry.

The Boiling Point of Aqueous Solutions of Nitric Acid at Different Pressures. II. The Influence of Water-retaining Agents on the Composition of the Mixture of Maximum Boiling Point. HENRY JERMAIN MAUDE CREIGHTON and HERSCHEL GASTON SMITH (*J. Franklin Inst.*, 1915, **180**, 703—709).—In continuation of earlier experiments (A., 1915, ii, 446), which showed that the composition of the maximum boiling mixture changes only from 66·80% of nitric acid at 110 mm. to 68·18% at 760 mm., the effect of the presence of potassium hydrogen sulphate and of sulphuric acid has been examined. The composition of the mixture of maximum boiling point is not appreciably altered by the addition of 10% or 20% of potassium hydrogen sulphate. On the other hand, sulphuric acid causes a decrease in the nitric acid content of the maximum boiling mixture, the decrease being greater the greater the addition of sulphuric acid. At 760 mm. the percentage of nitric acid in this mixture is reduced from 68·18 to 64·5 in presence of 10% of sulphuric acid and to 59·2 in presence of 20%. At lower pressures, the reduction in the nitric acid content is still larger.

The results obtained afford an explanation of the fact that solutions of nitric acid can be concentrated to more than 90% by distillation with concentrated sulphuric acid. H. M. D.

Two Reactions of Azoimide with Analytical Importance. FRITZ SOMMER and HEINRICH PINCAS (*Ber.*, 1915, **48**, 1963—1969, 2096).—A. *Oxidation of Azoimide by Ceric Salts.*—A method for the estimation of azoimide in neutral or acetic acid solutions by measuring the volume of the latent nitrogen was first proposed by Raschig in 1908, who found that when such a solution is mixed with a slight excess of iodine and a crystal of sodium thiosulphate, the evolution of nitrogen is brisk and complete (compare also following abstract). The authors find that although this method is trustworthy for $0·1N$-solutions, and therefore for solids, it is not so for very dilute solutions, the end of the reaction being reached too slowly. On the other hand, salts of quadrivalent cerium, such as ceric ammonium nitrate, ceric sulphate, or the ceric ammonium sulphates, immediately effect the complete oxidation of azoimide in neutral or acid solutions, even when these are very dilute, according to the equation $2N_3H + 2CeO_2 = 3N_2 + Ce_2O_3 + H_2O$. For 0·1 gram of the sodium salt about 2·3 grams of the cerium compound should be used. Free hydrochloric acid or excess of chlorine ions must be avoided, however, otherwise chlorine gas will be liberated.

B. *Reaction of Azoimide with Nitrous Acid.*—According to Thiele (A., 1908, ii, 940), azoimide reacts with nitrous acid thus: $N_3H + HNO_2 = N_2 + N_2O + H_2O$. The correctness of this assumption

has been proved by adding acetic acid to a mixture of equivalent quantities of barium nitrite and sodium azide and analysing the gases evolved. The reaction proceeds very smoothly and may be used to estimate simple nitrites. A known excess of sodium azide is added to an acidified solution of the nitrite, then the mixture is shaken for a minute or two, rendered just alkaline by barium hydroxide, and boiled to expel nitrous oxide, and finally acidified with acetic acid, when the excess of azoimide is estimated as above.

Another application of the reaction is the detection of nitric acid in the presence of nitrous. Nitrous acid is completely destroyed, even in a 0·0001*N*-solution, whilst nitric acid is unaffected, when a slight excess of sodium azide is added, the solution is acidified and boiled. This method for removing nitrous acid is much better than the old treatment with carbamide or the newer reaction with hydrazine sulphate (Sen and Dey, A., 1912, ii, 296). J. C. W.

Oxidation of Azoimide by Iodine. F. Raschig (*Ber.*, 1915, **48**, 2088—2092. Compare *Chem. Zeit.*, 1908, **32**, 1203).—The oxidation of azoimide by iodine in the presence of sodium thiosulphate might be regarded as a catalytic effect of sodium tetrathionate, as Sommer and Pincas have done (preceding abstract). This is not justifiable, however, for just as iodine alone causes no evolution of nitrogen, so a mixture of sodium tetrathionate with iodine is also without action.

If the reaction between iodine and sodium thiosulphate is considered, since no more than two molecules can react at any given instant, the first stage in the reaction will be represented thus: $Na_2S_2O_3 + I_2 = NaI + NaIS_2O_3$. It is this intermediate compound which so easily gives up iodine to the sodium azide (for example) or to another molecule of sodium thiosulphate, thus: $Na_2S_2O_3 + NaIS_2O_3 = Na_2S_4O_6 + NaI$. The actual catalyst is therefore the residue NaS_2O_3, which takes up iodine if that is in excess and gives it again to the azide, or, under normal conditions, condenses to form $Na_2S_4O_6$. Free mineral acids hinder the reaction, and since sulphuric acid is liberated as a by-product, it is advisable to add sodium acetate. Because of this effect of acids, it is always advisable, too, to keep adding sodium thiosulphate to the solution, and this is best effected by using a crystal about the size of a pea, which takes sufficiently long to dissolve.

Azoimide seems to be the only substance which, whilst unattacked by iodine alone, is oxidised by iodine in the presence of sodium thiosulphate. Bromine water and thiosulphate have the same effect, owing, no doubt, to the formation of $NaBrS_2O_3$. The only other iodine carrier which has been discovered among sulphur compounds is a sulphide. A crystal of sodium sulphide has the same effect, but the liberation of sulphur which also takes place renders the reaction less neat. J. C. W.

The Neutralisation Curve of Boric Acid. E. B. R. Prideaux (*Trans. Faraday Soc.*, 1915, **11**, 76—78).—A discrepancy is found

between the experimental neutralisation curve and that calculated from the single constant of a monobasic acid. This is attributed to the formation of complexes in the borate solutions, the ion H_2BO_3' being thus weighted by the complexes. A revised constant, $k = 4{\cdot}5 \times 10^{-10}$, is given, from which the alkalinity of borate solutions may be calculated up to strongly alkaline solutions.

C. H. D.

The Dissociation of Carbonyl Sulphide. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1915, **37**, 2786).—A correction of an error in sign in the recent paper by Lewis and Lacey (A., 1915, ii, 767). The modification thus introduced into the van't Hoff equation brings the calculated heat of formation of carbonyl sulphide from liquid sulphur and carbon monoxide to 11,000 cal., in good agreement with the value of Thomsen.

D. F. T.

The Supposed Formation of Persilicate by the Action of Air on Solutions of Sodium Silicate. HUGO DITZ (*J. pr. Chem.*, 1916, [ii], **92**, 412—418).—The author regards the statement that the solution of a silicate of an alkali metal when exposed to air undergoes partial oxidation to a persilicate (Jordis, A., 1914, ii, 200) as highly improbable. A solution of such a persilicate should actually contain the hydrolytic products, namely, a silicate and hydrogen peroxide, but the only evidence mentioned (*loc. cit.*) is the presence of a little free chlorine in the carbon dioxide liberated by hydrochloric acid. Such a result might be due to the presence of a little manganese as impurity in the silicate solution. However, the author (Ditz, also Ditz and Kanhäuser, A., 1913, ii, 958) has shown that after prolonged exposure to the air many alkaline substances are found to contain small quantities of nitrite and nitrate, and treatment with hydrochloric acid would give rise to nitrous fumes with the former, and, if the acid were concentrated, to chlorine with the latter. Experimental test has confirmed the possibility of this result with a solution of a silicate of an alkali metal, distinct traces of nitrite being present even after exposure for two days, the amount being very appreciable after three months. In the same period the quantity of nitrate formed was relatively small, whilst titanic acid failed to reveal any trace of hydrogen peroxide.

D. F. T.

Thermal Analysis of Mixtures of Alkali Hydroxides with the Corresponding Haloids. III. Lithium Compounds. GIUSEPPE SCARPA (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 476—482. Compare A., 1915, ii, 448, 633).—The systems LiOH–LiF, LiOH–LiCl, LiOH–LiBr, and LiOH–LiI have now been investigated. The lithium hydroxide employed contained 98·5% LiOH, 0·8% Li_2CO_3, and 0·7% H_2O, and had m. p. 462°; Dittmar (*J. Soc. Chem. Ind.*, 1888, **7**, 733) and de Forcrand (A., 1906, ii, 445) found m. p. 445°.

For lithium fluoride the author finds m. p. 840°; Carnelley (T., 1878, **33**, 281) gave 801°. Lithium hydroxide and fluoride are

completely miscible in the liquid state and form solid solutions containing from about 5 to 85 mols. % of the hydroxide. The eutectic point, 430°, corresponds with 80 mols. % of the hydroxide.

For lithium chloride, m. p. 605° is found. Guntz (A., 1894, ii, 91) gave 600°, Hüttner and Tammann (A., 1905, ii, 229) 600°, and Schemtschuschni and Rambach (A., 1910, ii, 204) 614°. The curve of primary crystallisation of the system LiOH–LiCl falls from 605° to a eutectic at about 290°, and exhibits a distinct angle at 50 mols. % LiOH. The eutectic arrest, observed at about 285° with all mixtures containing from 45 to 100 mols. % LiOH, has its maximum duration at about 65 mols. % LiOH. Mixtures containing 0—50 mols. % LiOH show a second arrest at 315°, this having its maximum duration for 40 mols. % LiOH, and corresponding with the formation of a compound, probably 2LiOH,3LiCl, decomposing on fusion.

Lithium bromide has m. p. 550°; Carnelley (*loc. cit.*) found 547°. The diagram of state for LiOH–LiBr is similar to that of the preceding system, the two branches of the curve of primary crystallisation intersecting at the eutectic point, 275°, which corresponds with 45 mols. % LiOH. The eutectic arrest is shown with 0—70 mols. % LiOH, but not with 75—100 mols. % LiOH; the latter mixtures exhibit, however, a marked arrest at 310°, this having its maximal duration with 75 mols. % LiOH, and corresponding with the formation of a decomposable compound, probably 3LiOH,LiBr.

Lithium iodide (probably containing a little oxide) has m. p. 440°; Carnelley (*loc. cit.*) found 446° and Sandonnini and Scarpa (A., 1914, ii, 204) 450°. The curve of primary crystallisation of the system LiOH–LiI exhibits a eutectic at 45 mols. % LiOH and a pronounced change of direction at 75 mols. % LiOH. The eutectic arrest occurs at about 180°, and is a maximum at 45 mols. % LiOH. Mixtures with more than 75 mols. % LiOH show an arrest at about 310°, probably owing to the formation of the compound 4LiOH,LiI, unstable at the melting point.

Comparison of these results with those previously obtained (A., 1915, ii, 448, 633) shows that the tendency of an alkali hydroxide to form compounds with the corresponding haloids increases with diminution of the electro-affinity of the cation (compare Abegg and Bodländer, A., 1899, ii, 542). T. H. P.

Preparation of Phosphorescent Calcium Sulphide. PIERRE BRETEAU (*Compt. rend.*, 1915, **161**, 732—733; *J. Pharm. Chim.*, 1916, [vii], **13**, 33—37).—Contrary to the views of Verneuil (compare A., 1887, 2, 539), it is shown that the presence of sodium chloride and carbonate in small quantities is not essential for the phosphorescence of calcium sulphide. A phosphorescent sulphide can be prepared by heating a mixture of calcium carbonate (100 parts) and powdered sulphur (30 parts) in a crucible at a dull red heat for one hour, allowing the mixture to cool, mixing it with alcohol to a paste, and adding basic bismuth nitrate in alcoholic solution in sufficient quantity to give 1 part of bismuth to 10,000

parts of sulphide. This mixture is dried in the air and then heated at a dull, cherry-red heat for two hours and allowed to cool slowly. The sulphide so prepared shows a violet phosphorescence. The bismuth, as phosphorogen, can be replaced by molybdenum or vanadium, or, better still, by tungsten. W. G.

The Derivatives of Perceric Oxide. II. C. C. MELOCHE (*J. Amer. Chem. Soc.*, 1915, **37**, 2645—2652).—It has not been possible to prepare perceric sodium carbonate by a method analogous to that used in the preparation of the potassium compound (A., 1915, ii, 776). A solution of perceric ammonium carbonate may be prepared by this method, but the substance has not been obtained in the crystalline form. The solution is less stable than that of the potassium compound, and decomposes when kept with the formation of a yellow precipitate, presumably ceric carbonate. If the dark red solution of perceric ammonium carbonate is treated with excess of solid sodium carbonate and the solution evaporated slowly in a vacuum, well-formed crystals of perceric sodium carbonate of the formula

$$Ce_2O_4(CO_3)_2,4Na_2CO_3,30H_2O$$

are obtained. It is only sparingly soluble in cold water and effloresces in dry air. Contact with moisture above 0° results in hydrolysis, and with larger quantities of water the crystals are completely decomposed with the formation of a gelatinous, orange-red precipitate.

A perceric rubidium carbonate was obtained in crystalline form by the method which served for the preparation of the potassium compound, but this substance has not been analysed.

The action of hydrogen peroxide on a saturated solution of potassium acetate in presence of cerous nitrate yields a solution which probably contains perceric potassium acetate. It liberates iodine from potassium iodide, gives a blood-red solution with potassium carbonate, and a reddish-brown precipitate with hydrogen peroxide. In all these perceric compounds, half the total oxygen combined directly with the cerium is available for oxidation under certain conditions. H. M. D.

Some New Rare Earth Compounds. A. J. GRANT and C. JAMES (*J. Amer. Chem. Soc.*, 1915, **37**, 2652—2654).—With a view to the improvement of the methods employed in the separation of the rare earths, a number of new salts have been prepared. Terbium pyromucate, $(C_4H_3O\cdot CO_2)_3Tb,5H_2O$, radiating crystals, very soluble in water; terbium 1-bromo-2-nitrobenzene-4-sulphonate, $(NO_2\cdot C_6H_3Br\cdot SO_3)_3Tb,10H_2O$, very small crystals, the solubility of which differs little from that of the gadolinium salt; terbium propionate, $(C_2H_5\cdot CO_2)_3Tb,2H_2O$, white, powdery, voluminous crystals; ferrous lanthanum nitrate, $3Fe(NO_3)_2,2La(NO_3)_3,24H_2O$, flat, green, hexagonal crystals, fairly stable in the absence of air. Lanthanum pyromucate, $(C_4H_3O\cdot CO_2)_3La,2H_2O$; and yttrium pyromucate, $(C_4H_3O\cdot CO_2)_3Yt,3H_2O$, were also prepared. H. M. D.

The Separation of Yttrium from the Yttrium Earths. III. J. P. BONARDI and C. JAMES (*J. Amer. Chem. Soc.*, 1915, **37**, 2642—2645. Compare A., 1914, ii, 370, 657)—Further experiments have been made with the object of finding a rapid, efficient, and economical method for the separation of yttrium from the yttrium earths The results of fractional precipitation by the addition of various reagents are briefly described. These reagents include ammonium sebacate, azcbenzenesulphonic acid, potassium sulphite, sodium citrate, tartrate, tungstate, phenoxyacetate, and *m*-nitrobenzoate, ammonium camphorate, and potassium cobalticyanide. The use of a cobalticyanide solution appears the most promising for the purposes of the required separation, and this method is to be further examined. H. M. D.

Decomposition of Mineral Sulphides and Sulpho-salts by Thionyl Chloride. H. B. NORTH and C. B. CONOVER (*Amer. J. Sci.*, 1915, [iv], **40**, 640—642. Compare this vol., ii, 28).—Mineral sulphides react, in general, in a similar manner to the precipitated sulphides with thionyl chloride according to the general scheme $MS + 2SOCl_2 = MCl + SO_2 + S_2Cl_2$. The reactions take place at 150—175°, and require from a few hours' heating in the case of easily decomposed sulphides, such as galena, pyrites, cinnabar, orpiment, stibnite, and arsenical pyrites, to one or two days in the case of pyrargyrite, proustite, covellite, sphalerite, and tetrahedrite. Of the minerals examined, only argentite, molybdenite, and cobaltite were not attacked by thionyl chloride under the above conditions. G. F. M.

Reaction of Gases with Lead and Silver. W. STAHL (*Chem. Zeit.*, 1915, **39**, 885—886).—A summary of published work on the behaviour of lead and silver at high temperatures towards oxygen, sulphur dioxide, hydrogen, nitrogen, the oxides of carbon, hydrocarbons, argon, and helium. G. F. M.

Supposed Allotropy of Copper. G. K. BURGESS and I. N. KELLBERG (*J. Washington Acad. Sci.*, 1916, **5**, 657—662).—From dilatometric observations, Cohen and Helderman (A., 1914, ii, 205, 654) have drawn the conclusion that there are two enantiotropic forms of copper with a transition temperature at 69·2° to 71·7°. In support of this view, the change in the electrical conductivity of copper after heating at 100° has been put forward.

Comparative measurements made with copper and platinum wire resistance thermometers wound on the same frame and exposed alternately to 0° and 100°, show that platinum exhibits similar changes in conductivity, and that in both cases constancy is obtained after a few alternations of temperature. A detailed examination of the resistance of copper over the range 0° to 100°, by the method described in a previous paper (A., 1914, ii, 794), has also given entirely negative results in respect of the alleged allotropic transformation in the neighbourhood of 70°. Within the above range, the resistance of copper changes in a continuous

manner, and there is no evidence of the copper being in a metastable condition. H. M. D.

Sulphides of Copper. EUGEN POSNJAK, E. T. ALLEN, and H. E. MERWIN (*Economic Geology*, 1915, **10**, 491—535).—A general physico-chemical investigation of the sulphides of copper and of the various copper-iron sulphide minerals, carried out with the object of ascertaining the conditions of formation and alteration of the more important minerals of the copper sulphide deposits. Cuprous sulphide prepared in a vacuum furnace has m. p. 1130° ± 1°. No dissociation occurs when cuprous sulphide is heated up to 1200°. Synthetic cuprous sulphide has $D_{4°}^{25°}$ 5·785, a value which is almost identical with that of the purest mineral sulphide examined. The copper sulphides formed by fusing together copper and sulphur are of variable composition and always contain more sulphur than is demanded by the ratio 2Cu : S. They are microscopically homogeneous and vary continuously both in colour and specific gravity with composition. As the sulphur increases, they become darker in colour and have smaller specific gravities. The specific volumes of these products lie, within the limits of experimental error, on a straight line connecting the specific volumes of cuprous and cupric sulphides. It is shown that all such products are solid solutions of the two sulphides. Cuprous sulphide melts at 1096° in an atmosphere of hydrogen sulphide and at 1057° in an atmosphere of sulphur vapour. The lower melting point as compared with that of cuprous sulphide in a vacuum is due to dissolved cupric sulphide, which increases in amount with the increase of pressure of the sulphur vapour surrounding it. When cuprous sulphide is heated in an atmosphere of hydrogen sulphide at various temperatures below its melting point, the sulphur content increases. For each temperature, the products contain a definite amount of sulphur. This sulphur content increases with decrease of temperature until at 358° the product becomes cupric sulphide. Solid solutions of cuprous-cupric sulphide can be prepared by heating compressed powders of the two sulphides at about 100°. The analysis of a number of natural chalcocites showed that such solid solutions sometimes occur in nature. In this connexion, the nature of the mineral pyrrhotite has been discussed. Cuprous sulphide is dimorphous and has an inversion temperature at 91°. The inversion temperature is considerably influenced by the size of the grains of the sulphide. Increasing amounts of cupric sulphide, dissolved in cuprous sulphide, raise the inversion temperature. This takes place until a concentration of cupric sulphide of 8% is reached, after which an inversion is no longer observed. Crystals of chalcocite were repeatedly formed in the dry way at various temperatures, but only above about 250° were they large enough for crystallographic investigation. These crystals were isometric. Isometric crystals of cuprous sulphide were also obtained from solutions; at 250°, by the reaction of cuprous chloride with sodium sulphide; and at 200°, 170°, and 125°, by crystallisation of cuprous sulphide from solutions of hydrogen sulphide. Crystals formed by

the action of ammonium sulphide on copper, which have generally been described as orthorhombic cuprous sulphide, are in reality a double polysulphide of the formula $Cu_7(NH_4)S_4$ and are tetragonal. Covellite has been prepared in many ways, and a crystallographic and optical study of its properties carried out. It is hexagonal and optically positive; the optical dispersion of ω is extremely high, $\omega_{Li} < 1{\cdot}0$, $\omega_{Na} = 1{\cdot}45$, and $\omega_{Tl} = 1{\cdot}80$. Two very pure samples of covellite have been found to have D_4^{25} 4·683 and 4·676 respectively. This value is higher than any value previously given for this substance. The highest value found for synthetic covellite was 4·652. Covellite can be heated in an atmosphere of hydrogen sulphide up to 358°; it is then in equilibrium with the gas, and at this temperature and below it, chalcocite can be completely converted into covellite. J. F. S.

The Nature of Subsidiary Valencies. XII. Ammines of Copper. FRITZ EPHRAIM and EDOUARD BOLLE (*Ber.*, 1915. **48**, 1770—1777. Compare A., 1915, ii, 166, 441, 454).—Details are given of the preparation of various ammines of copper salts, in addition to those previously described; the ammonia tension has also been measured at various temperatures.

The cupric salts of dibasic acids in no case give a hexammine compound, even at the temperature of an ice-salt freezing mixture, the highest ammine formed being the pentammine. Many of the salts of monobasic acids give a hexammine compound. In many cases where the hexammine is capable of existence only at very low temperatures, the triammine is nevertheless stable at fairly high temperatures. The order in which the anions exert an effect on the stability of the ammine is quite different from that observed in the case of the nickel salts; it resembles rather that observed with the zinc salts (A., 1915, ii, 454), although with many differences. The theoretical discussion of the results is to be given later.

The following new compounds are described: *Copperhexammine nitrate*, blue crystals; the ammines with 5 and 23/4 molecules of ammonia, which have been described by other investigators, could not be obtained. *Copperhexammine perchlorate*. *Copperpentammine dithionate*; the ammine with 9 molecules of ammonia could not be obtained. *Coppertetrammine tetrathionate*, light blue crystals; *copperhexammine thiocyanate*; *coppertetrammine formate*; *coppertriammine benzoate*, copper-red crystals; *coppertetrammine benzoate*, dark blue crystals; and *copperpentammine benzoate*, greyish-blue crystals.

The ammonia tensions of the following salts were also determined: coppertetrammine nitrate, coppertetrammine thiosulphate, coppertetrammine dithionate, coppertetrammine thiocyanate, and copperpentammine oxalate.

A table is given showing the absolute dissociation temperatures and the heats of formation of all the copper ammines hitherto examined. T. S. P.

Thermal Reactions of Aluminium. RAFAEL LUNA NOGUERAS (*Anal. Fis. Quim.*, 1915, **13**, 390—420).—A historical account of

the production of aluminium, and of its applications as a thermal agent. A. J. W.

Investigation of the Carbides of Aluminium, Nickel, and Copper. E. BRINER and R. SENGLET (*J. Chim. Phys.*, 1915, **13**, 351—375).—A study of the conditions under which carbon combines directly with the three metals, and of the dissociation of the resulting carbides.

The formation of aluminium carbide from the elements has been observed at 750° and 900°. This compound is exothermic and represents, therefore, the stable form at lower temperatures. Dissociation of the carbide was found to occur, however, at 540°, and when heated in a current of air, carbon dioxide and aluminium oxide are obtained. This change has been followed at various temperatures between 540° and 900°.

Nickel carbide, Ni_3C, is an endothermic compound, and the optimum temperature of formation is in the neighbourhood of 2100°. At lower temperatures, the carbide dissociates, relatively rapidly at 1600°, and slowly at 900°. The carbide must consequently be cooled rapidly if a good yield is required.

Some evidence has been obtained of the direct combination of copper and carbon to form a carbide at high temperatures. It is endothermic and dissociates rapidly at about 1600°, more slowly at lower temperatures. H. M. D.

Identification of Tervalent Manganese in Glass. S. R. SCHOLES (*J. Ind. Eng. Chem.*, 1915, **7**, 1037).—The author considers that the violet tint of manganese glass is due to compounds of the trioxide, Mn_2O_3, deducing as evidence in support of this theory the fact that pink solutions were obtained by extracting a lead glass of low m. p. and a water-soluble potash glass with hydrofluoric or 30% sulphuric acids. On diluting the extracts with water, a light brown precipitate separated out similar to that obtained by diluting a manganic sulphate solution. Their behaviour towards oxalic acid was also the same. G. F. M.

A Magnetic Study of the A3 Transformation in Pure Iron. KÔTARÔ HONDA and HIROMU TAKAGI (*Sci. Rep. Tohoku Imp. Univ.*, 1915, [ii], **4**, 261—269).—Four different specimens of pure iron from the Bureau of Standards, Washington, have been examined thermomagnetically. The specimens, weighing about 0·4 gram, are tested in an atmosphere of nitrogen. Both the beginning and end of the transformation may be readily traced on the curves, and the critical points thus determined are in good agreement with those found by thermal analysis. The magnetic value of Ac3 for pure iron is 908—911°, and of Ar3 889—898°. The number of magnetons is not usually an integer, and varies for different specimens. These facts are opposed to Weiss's theory. C. H. D.

The Magnetic Transformation of Cementite. KÔTARÔ HONDA and HIROMU TAKAGI (*Sci. Rep. Tohoku Imp. Univ.*, 1915, [ii], **4**, 161—167).—A thermal and magnetic examination of a series

of white pig irons containing from 2·90% to 3·49% of combined carbon shows that the magnetic transformation of cementite begins on cooling at 215°, and ends on heating at the same temperature. The temperature range is about 50°. The magnitude of both the thermal and magnetic changes increases with the proportion of cementite. It is small in a grey iron. The critical temperature is the same in steels containing as little as 0·14% of carbon, so there is no indication of the presence of more than one carbide.

C. H. D.

Presence of Platinum in Spain. S. Piña de Rubies (*Anal. Fis. Quim.*, 1915, **13**, 420—433).—A summary of the records as to the occurrence of platinum deposits in Spain. A. J. W.

The Series of Triamino-aquo Salts of Bivalent Platinum, $[Pt3NH_3,H_2O]X_2$. L. Tschugaev and I. Tschernjaev (*Compt. rend.*, 1915, **161**, 792—794. Compare this vol., ii, 42).—On passing a current of air through a solution of the chloride,

$$\left[\begin{matrix}NH_3\\OH\cdot NH_2\end{matrix}>Pt<\begin{matrix}NH_2\cdot OH\\NH_3\end{matrix}\right]Cl_2,$$

containing ammonia and ammonium sulphate, or any other sulphate, and a small amount of any copper salt, oxidation occurs, a colourless, crystalline precipitate being obtained which is soluble in warm dilute sulphuric acid. Addition of potassium platinochloride to this acid solution gives a precipitate of the *platinochloride*, $[Pt3NH_3,H_2O]PtCl_4$, green needles, which when warmed with hydrochloric acid or a soluble chloride is converted into Cleve's platinochloride, $[Pt3NH_3,Cl]_2PtCl_4$. Addition of potassium platinobromide to the acid solution gives the *platinobromide*,

$$[Pt,3NH_3,H_2O],PtBr_4,$$

green needles, which is converted by hydrobromic acid or soluble bromides into the platinobromide, $[Pt3NH_3,Br]_2,PtBr_4$. Analysis of the original oxidation product points to its composition being represented by the formula

$$\left[4NH_3Pt<\begin{matrix}OH\\OH\end{matrix}>Pt4NH_3\right]SO_4,$$

in which case it is allied to Werner's binuclear diol complexes, the index of co-ordination of the platinum being equal to 6. W. G.

The Series of Hydroxy-pentamminoplatinic Salts. L. Tschugaev and W. Chlopin (*Compt. rend.*, 1915, **161**, 699—700. Compare Tschugaev and Vladimirov, A., 1915, ii, 569).—The authors have prepared a series of salts having the general formula $[Pt,5NH_3,(OH)]X_3$. The *carbonate* is readily prepared by passing a current of ozone through a mixture of Peyrone's chloride (1 part) and ammonium carbonate (2 parts) in an excess of ammonia for two or three hours with continual stirring. The carbonate is precipitated, being insoluble in water, and is readily decomposed by acetic acid, giving the *acetate*,

$$[Pt,5NH_3,(OH)](CH_3\cdot CO_2)_3.$$

This salt in solution is decomposed by mineral acids to give the corresponding salts. In this way the *chloride*,

$$[Pt,5NH_3,(OH)]Cl_3,H_2O,$$

rhombic plates, and the *nitrate*, $[Pt,5NH_3,(OH)](NO_3)_3$, crystallising in anhydrous needles, were prepared. Both these salts are soluble in water and are ionised. The hydroxyl group, like the chlorine atom in the series $[PtCl,5NH_3]X_3$, is completely masked and apparently not capable of being directly replaced by a halogen or any other negative atom or group. That the group

$$[Pt,5NH_3,(OH)]'''$$

is tervalent is shown by a study of the coagulating power of the chloride, the results of which agree with those of the luteocobaltammines, which give by dissociation tervalent ions. Like the members of the series $[Pt,5NH_3,Cl]X_3$ and the series $[Pt,6NH_3]X_3$, the salts of this series give carbonates and sulphates which are practically insoluble in water, but soluble in the fixed alkalis. Further, the chlorides of all these three series are readily reduced by zinc in dilute hydrochloric acid, giving in each case the chloride of Reiset's base I, $[Pt,4NH_3]Cl_2$. W. G.

Mineralogical Chemistry.

Muscovite with Unusual Optical Characters from a Marble in Maryland. R. W. CLARK and W. F. HUNT (*Centr. Min.*, 1915, 666—668).—A greyish-brown dolomitic marble, known in the trade as "Mar Villa" marble, occurs in large quantity at Cockeysville, Maryland. It owes its colour to the presence of a brown mica, which has the optical characters of phlogopite (markedly pleochroic; optic axial angle very small and optic axial plane parallel to the plane of symmetry), but the chemical composition of muscovite (the ratio $Al_2O_3:SiO_2$, as shown in the following bulk analysis of the marble, being nearer to that of muscovite, 1 : 2, than to that of phlogopite, 1 : 6).

SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	MnO.	CO_2.	FeS_2.	Total.
3·88	1·24	0·32	30·06	20·41	0·02	43·93	0·06	99·92

The percentage mineralogical composition calculated from this bulk analysis of the marble is: dolomite (with MgO : CaO = 1 : 1·1), 93·97; muscovite, 2·27; tremolite, 3·75; pyrites, 0·06. L. J. S.

Analytical Chemistry.

Theory of Indicators Used in Acidimetry. RUD. WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1915, **90**, 641—680).—A theoretical paper in which a theory of indicators is developed on the assumption that undissociated compounds and their ions, when these have the same constitution as the parent substance, are similarly coloured, and all colour changes are to be ascribed to constitutional changes. Formula are deduced which give the concentration of free acid or base at stated hydrogen ion and indicator concentration, and also the concentration of the indicator which must be employed in order exactly to titrate such a solution. The author differentiates between ideal and non-ideal indicators. The ideal indicators are those for which the one form occurs only in the ionised condition and the other form in the non-ionised condition. In the case of single coloured indicators the ideal indicators behave differently from the non-ideal indicators. Ideal indicators increase in sensitiveness with concentration, whereas with non-ideal indicators a maximum of sensitiveness appears at a definte concentration. Non-ideal indicators generally are less sensitive than ideal indicators, except that just at the equivalent point the advantage of the ideal indicator over the non-ideal is very small. For the calculation of all data it is necessary in the case of single colour indicators to have knowledge of the apparent dissociation constant of the colourless indicator and the real dissociation constant of the coloured form. For titration to the point of equivalence, in alkaline solution coloured indicator acids are better than coloured indicator bases, and in the same way in acid solution coloured indicator bases are better than coloured indicator acids. Indicators with two colours behave in different ways. The behaviour in all cases can be completely represented from the apparent dissociation constant. Ideal and non-ideal two-coloured indicators behave similarly. The equilibrium constants, that is, the dissociation constants of both forms and the reaction constant of the change from one form to the other, of non-ideal indicators can only be determined by the usual chemical and optical methods when a spectral region exists in which only one form absorbs light.

J. F. S.

Apparent Transformation of Indicators. F. LIEBERT (*Chem. Weekblad*, 1915, **12**, 1088—1091). Compare de Vries, this vol., i, 56).—The author cites a number of examples of colour change of indicators before titration is complete. A. J. W.

Testing Distilled Water as Regards its Suitability for the Preparation of Salvarsan Solutions. J. TILLMANS and H. MILDNER (*Zeitsch. angew. Chem.*, 1915, **28**, 469—474).—The distilled water used for preparing salvarsan solutions for injections

should be free from large numbers of bacteria, soluble constituents of glass, and heavy metals. The presence of a large number of bacteria in the water is usually indicated by a high oxygen absorption (from permanganate) and by the presence of ammonia and nitrous acid, and estimations of these will afford evidence of the suitability of the water, apart from an actual bacteriological analysis. One hundred c.c. of the water when boiled with $N/100$-permanganate solution in the presence of dilute sulphuric acid should not reduce more than 0·2 c.c. of the permanganate solution; ammonia and nitrous acid should not be present. Provided that the distilled water is not contaminated by tap-water, as is shown by the absence of chlorine, nitric acid, and calcium, the presence of soluble constituents of glass is indicated by the appearance of a red coloration when the boiled water is treated with a few drops of rosolic acid solution. The presence of traces of iron in the water is not of importance; tin is not dissolved by distilled water, but tests should be applied for the detection of lead, copper, nickel, and zinc. W. P. S.

Persistence of Hydrogen Peroxide in Milk. E. HINKS (*Analyst*, 1915, **40**, 482—489).—It was found that hydrogen peroxide when added to milk was destroyed rapidly at first, that the rate of destruction diminished, and that if the concentration of the hydrogen peroxide was high enough to withstand the initial rapid destruction, the residual peroxide remained constant in amount over long periods (up to eighteen months). The age of the milk was the most important factor in regard to its behaviour towards hydrogen peroxide; fresh milk had the least effect, whilst milk three days old, and in which the catalytic activity had increased considerably, was capable of destroying relatively large quantities of hydrogen peroxide within one hour. The rate at which the hydrogen peroxide was decomposed increased with the temperature up to 37°. In the case of a sample of fresh milk in which the initial concentration of hydrogen peroxide was 0·2%, about 33% of the peroxide was still present after the lapse of one year. It is pointed out that, owing to the destruction of peroxydase by hydrogen peroxide, it is necessary when testing for the presence of the latter to add some fresh milk as well as the reagent (benzidine, *p*-phenylenediamine, etc.) in order to ensure the presence of peroxydase; the addition of fresh milk is also necessary in testing heated milk for the presence of hydrogen peroxide. The possibility of a milk having received an addition of hydrogen peroxide must be considered when these reactions are used for the detection of previous heating, since a milk containing peroxide will react in certain circumstances in exactly the same way as a heated milk. W. P. S.

Estimation of Bromine and Iodine in the Presence of Chlorides. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1915, **28**, 477—480, 494—496).—In the case of bromides containing but small quantities of chlorides, the bromine may be estimated by

acidifying the bromide solution with sulphuric acid and titrating the boiling mixture with permanganate solution, the latter being added in small quantities at a time until a pink coloration remains on boiling the mixture for about one minute. If large quantities of chloride are present, the bromide solution is titrated in a flask attached to a condenser, the end-point of the titration being denoted when the drops of distillate no longer exhibit a yellow colour due to the presence of bromine. In the case of sea-water, a portion of the sample is placed in a flask, acidified with sulphuric acid, and distilled, with the continual addition of small quantities of permanganate solution. The distillate is collected in sulphur dioxide solution, hydrogen peroxide solution, or alkali hydroxide solution, and the resulting hydrobromic acid or hypobromite is then estimated by the usual methods. For the estimation of iodine in the presence of bromides and chlorides, the sodium nitrite method is recommended. The sample is acidified and shaken with sodium nitrite solution in the presence of carbon tetrachloride; after several of these treatments the separated carbon tetrachloride solutions are treated with carbamide to decompose traces of nitrite, and then titrated with thiosulphate solution. Bromine may be estimated, if present, in the same portion of the sample. For this purpose, the solution remaining after the separation of the carbon tetrachloride is acidified with sulphuric acid, distilled until dissolved carbon tetrachloride and nitrous acid have been expelled, and then titrated with permanganate solution as described. W. P. S.

New Method of Estimating Iodine in Organic Preparations. E. Rupp and F. Lehmann (*Arch. Pharm.*, 1915, **253**, 443—451).—The method depends on the fact that chlorine and bromine in organic preparations are removed in the elementary state by heating with sulphuric acid and potassium permanganate in the presence of a silver salt, whilst iodine is retained in the form of silver iodate, provided an excess of permanganate is always present.

Twenty c.c. of concentrated sulphuric acid and 25 c.c. of $N/10$-silver nitrate are heated in a 500 c.c. Kjeldahl flask until the flask is filled with white fumes. The mixture is then cooled, 2·5 grams of finely powdered potassium permanganate are added, and a small glass tube containing the substance (0·25 gram) is allowed to slide into the mixture. In those cases in which a vigorous evolution of gas does not ensue by shaking, 5 c.c. of water are added immediately; in the contrary cases, the addition of the water is postponed until the vigorous reaction has almost ceased. After the addition of the water the mixture is vigorously shaken for one to two minutes, and is then kept for fifteen minutes with frequent shaking. The flask is then closed with a filter-funnel and heated in a sloping position, at first gently until the liquid boils, then strongly. By repeated rotation of the flask any particles of substance or of manganese dioxide carried into the neck are washed back into the liquid. The heating is maintained until the manganese dioxide has been almost entirely decomposed and a deep blue solution has been obtained. This is thoroughly cooled,

treated with a freshly-prepared solution of 5 grams of crystallised ferrous sulphate in 100 c.c. of water, and is vigorously shaken for a few minutes until the silver iodide has curdled and the supernatant liquid is quite clear. The contents of the flask are then washed into a large beaker and the excess of silver is titrated with $N/10$-thiocyanate.

In some cases less energetic treatment suffices to decompose the organic preparation. For example, 0·5 gram of airol (bismuth gallate iodide) is boiled for two to three minutes with 20 c.c. of 25% nitric acid and 20 c.c. of $N/10$-silver nitrate, the mixture is diluted with 50 c.c. of water and allowed to cool, a little potassium permanganate is added to oxidise any nitrous acid and then ferrous sulphate until the red colour has disappeared, and the excess of silver is titrated with $N/10$-thiocyanate; not more than 12·1 c.c. of the last (=20% of iodine) should be consumed. C. S.

Absorption of Oxygen in Alkaline Solutions, and a New Absorbent for Oxygen. F. HENRICH (*Ber.*, 1915, **48**, 2006—2009). —When studying the autoxidation of orcinol (A., 1915, i, 564), the author noticed that the reaction proceeded much more quickly in the presence of potassium hydroxide than in the presence of sodium hydroxide. In connexion with other work involving the estimation of oxygen in gaseous mixtures, the relative value of the two alkalis has been tested in the common absorbents. It is found that sodium hyposulphite or pyrogallol solutions are more efficient when made up with potassium hydroxide than with the equivalent of sodium hydroxide.

The very concentrated alkaline solutions of pyrogallol are sometimes unsuitable, and therefore the author has sought for another absorbent among the trihydroxybenzenes. An excellent solution, far surpassing pyrogallol in activity and stability, is made as follows: 11·4 grams of crude, powdered hydroxyquinol triacetate, prepared by the action of acetic anhydride on *p*-benzoquinone (Thiele, A., 1898, i, 469), is suspended in 20 c.c. of water, shaken in a hydrogen atmosphere with a concentrated alkali hydroxide containing 17·4 grams of KOH or the equivalent (6 mols.) of NaOH, and then the solution is diluted in the pipette with 130 c.c. of water. J. C. W.

Titration of Thiosulphates in the Presence of Sulphides and the Estimation of Thiosulphates in the Presence of Sulphites, Bisulphites, and Sulphides. A. SANDER (*Chem. Zeit.*, 1915, **39**, 945—947. Compare A., 1915, ii, 161).—A method for the estimation of thiosulphate and sulphide when present in the same solution depends on their different behaviour towards mercuric chloride. When mercuric chloride is added to sodium sulphide solution, a black precipitate of mercuric sulphide at first forms which, on the further addition of mercuric chloride, changes to white mercuric thiochloride: $3HgCl_2 + 2Na_2S = 4NaCl + (2HgS,HgCl_2)$; sodium thiosulphate reacts with mercuric chloride according to the equation

$$2Na_2S_2O_3 + 3HgCl_2 + 2H_2O = 2Na_2SO_4 + 4HCl + (2HgS,HgCl_2).$$

An aliquot portion of the solution containing the two salts is titrated with $N/10$-iodine solution; another portion of the solution is then treated with an excess of mercuric chloride, ammonium chloride is added, and the mixture titrated with $N/10$-sodium hydroxide solution, using methyl-orange as indicator. The number of c.c. of alkali solution used divided by 2 gives the quantity of $N/10$-iodine solution required for the thiosulphate, and the difference between the two titrations corresponds with the iodine required for the sulphide. A method described by Bosshard and Grob (A., 1913, ii, 525) may be used for the estimation of thiosulphate in the presence of sulphite. An alternative method consists in titrating the two salts with iodine solution; another portion of the sample is then treated with mercuric chloride, and the acidity formed from the thiosulphate titrated with alkali solution. The reaction between sulphites and mercuric chloride is shown by the equation: $Na_2SO_3 + HgCl_2 = NaCl + HgCl{\cdot}NaSO_3$. For the estimation of thiosulphate, sulpide, and sulphite in the presence of each other a definite volume of the solution containing these salts is added to an excess of $N/10$-iodine solution previously acidified with 10 c.c. of $N/10$-hydrochloric acid, and the excess of iodine is titrated with $N/10$-thiosulphate solution; let A be the number of c.c. of iodine solution used. The same solution is then titrated with $N/10$-sodium hydroxide solution, using methyl-orange as indicator; after deducting the 10 c.c. of $N/10$-hydrochloric acid added previously, the result corresponds with the quantity of $N/10$-iodine solution (B) required for the sulphite. Another equal portion of the original solution is now treated with an excess of mercuric chloride, ammonium chloride is added, and the acidity of the mixture is titrated with $N/10$-sodium hydroxide solution (C); the ammonium chloride is added to prevent precipitation of mercuric oxide by the alkali. Then, the amount of $N/10$-iodine solution used by the thiosulphate is $C/2$, for the sulphite B, and for the sulphide $A-(B+C/2)$. A mixture consisting of 0·2471 gram of $Na_2S_2O_3$, 0·1249 gram of Na_2SO_3, and 0·1207 gram of Na_2S was analysed by this method, with the following results: $Na_2S_2O_3$, 0·2483 gram; Na_2SO_3, 0·1261 gram; Na_2S, 0·1201 gram.

W. P. S.

Estimation of Ammonia Nitrogen in Steer's Urine. DONALD C. COCHRANE (*J. Biol. Chem.*, 1915, **23**, 311—315).—Figures for nitrogen as free ammonia in the urine of cattle are untrustworthy, because of the decomposition of ammonium carbonate, and special precautions must be adopted to overcome this rapid decomposition; chloroform and toluene fail to prevent it. Sulphuric acid, added to the urine of a steer in quantity sufficient to fix the ammonia present as carbonate, and to slight excess, retards decomposition to such an extent as to allow time for analysis.

W. D. H.

A Source of Error in the Analysis of Coal which Contains Large Quantities of Alkaline Earth Carbonates. KNUBLAUCH (*Zeitsch. angew. Chem.*, 1915, **28**, 492—494).—Attention is directed

to the fact that, during combustion, calcium and magnesium carbonates, when present in a coal, evolve carbon dioxide, and that the latter is absorbed in the potash bulbs, thus causing the result for carbon to be too high. When oxygen is estimated by difference, an error is introduced of the ash of the coal is not treated with ammonium carbonate and again ignited gently before being weighed. Unless the necessary corrections are made for these errors, the true calorific value of a coal cannot be calculated from the results of the elementary analysis of the sample. W. P. S.

Estimation of Carbon Dioxide and a New Form of Absorption Tower Adapted for the Titrimetric Method. E. TRUOG (*J. Ind. Eng. Chem.*, 1915, **7**, 1045—1049).—The methods available for the estimation of carbon dioxide are reviewed. The gravimetric method, by weighing absorption apparatus, gives good results only when aspiration is slow; when large amounts of carbon dioxide are in question, the method is troublesome. The titrimetric method of absorption in alkali hydroxide and double titration has the disadvantage of uncertain end-points. The author recommends absorption in barium hydroxide solution in a special absorption tower consisting essentially of a suction flask, into the neck of which a fairly wide glass tube about 2 feet long, extending to within 1/8th-inch of the flask, and two-thirds full of glass beads, is fixed. The top of the tube is closed with a cork through which passes a 50 c.c. dropping funnel and a tube leading to the aspirator, the funnel being closed with a soda-lime tube. In use, the tower is first freed from carbon dioxide in the usual way, the funnel is charged with standard baryta solution, which is allowed to run over the beads in the glass tube, thus producing efficient contact between the solution and the carbon dioxide, which is aspirated fairly rapidly into the suction flask through its side aperture, and so up the tower. Absorption being complete, the baryta solution is washed into the suction flask and rapidly titrated. G. F. M.

Apparatus for Measuring the Carbon Dioxide Evolved During Alcoholic Fermentation. L. LINDET (*Ann. Falsif.*, 1915, **8**, 295).—The apparatus described consists of a glass cylinder, such as is used for drying gases, having a tubulure at the bottom; this tubulure carries a side tube which is bent upwards and then downwards at a height of about 4 cm. below the top of the cylinder. The neck of the cylinder is closed with a rubber stopper through which pass the delivery tube from the fermentation flask and a short length of tube; the upper end of this tube passes through a cork which closes the neck of an inverted flask. The cylinder and the flask are filled with light petroleum. As the carbon dioxide collects in the upper part of the cylinder, an equivalent volume of "petrol" is discharged through the side tube and is collected in a graduated cylinder; its volume is equal to that of the evolved carbon dioxide. The light petroleum in the inverted flask serves to keep the level of the light petroleum in the cylinder constant.

W. P. S.

Practical Methods for the Determination of Radium. II. The Emanation Method. S. C. LIND (*J. Ind. Eng. Chem.*, 1915, **7**, 1024—1029. Compare A., 1915, ii, 486).—A detailed description is given of a number of methods of chemical treatment designed with the object of preparing emanation from radium ores and residues, obtained in the commercial production of radium, for measurement in the electroscope previously described. The emanation may be removed either from a solution or from a fusion. In the former case, excess of barium and a rather high concentration of nitric acid must be maintained in order to prevent, as far as possible, the formation of radium sulphate, from which the emanation is only expelled with great difficulty. The boiling off is conducted in a special apparatus consisting essentially of a flask connected with a gas burette charged with hot sodium hydroxide solution, and leading from its upper end into the electroscope chamber. When the radio-active substance is insoluble in water or acids, fusion with alkali carbonate is resorted to, and in many cases the emanation may be expelled from the fused product by dissolving it in nitric acid in the flask of the above-mentioned apparatus. G. F. M.

Estimation of Potassium in Potassium Salts by the Perchlorate Method. G. HAGER and J. KERN (*Landw. Versuchs-Stat.*, 1915, **87**, 365—380).—Investigation of this method (compare A., 1914, ii, 817) showed that the solubility of potassium perchlorate in alcohol increases as the strength of the alcohol decreases. The presence of perchloric acid and of barium, sodium, and magnesium perchlorates decreases the solubility of the potassium salt. Alcohol of at least 96% by vol., and containing up to 1% of perchloric acid, should be used for washing the potassium perchlorate when dealing with a fairly pure potassium salt. A concentrated alcoholic solution of perchloric acid should be used in the preparation of the alcoholic solution of this acid employed for washing the potassium perchlorate. The method yields low results when applied to the estimation of potassium in samples containing much sulphate, owing to the fact that potassium salts are occluded in the barium sulphate during the necessary preliminary removal of sulphates; other methods for the estimation should be used for such samples [compare Thin and Cumming, T., 1915, **105**, 361; Davis, *ibid.*, 1679]. W. P. S.

Perchlorate and Cobaltinitrite Methods for the Estimation of Potassium. T. D. JARRELL (*J. Assoc. Official Agric. Chem.*, 1915, **1**, 29—32; from *J. Soc. Chem. Ind.*, 1915, **34**, 1170).—The author has applied these methods to the estimation of potassium in potassium chloride and in fertilisers, and finds that neither method is satisfactory in its present form. J. C. W.

Electro-analysis of Silver Without Platinum Electrodes. J. GUZMÁN and J. ALEMANY (*Anal. Fis. Quim.*, 1915, **13**, 343—350). —An account of results obtained in the electro-deposition of silver

on a nickel-plated copper cathode. The anode consisted either of passive iron or graphite. A. J. W.

Estimation of Silver in Organic Preparations. J. Herzog (*Arch. Pharm.*, 1915, **253**, 441—442).—Lehmann's method (A., 1915, ii, 650) is recommended. Two grams of potassium permanganate may, in general, be regarded as a suitable amount of the oxidising agent, but the optimum quantity for each individual preparation must be determined by experience. C. S.

Volumetric Estimation of Cadmium and Zinc. Henrik Enell (*Zeitsch. anal. Chem.*, 1915, **54**, 537—546).—When cadmium sulphide is shaken for some time with an excess of iodine, reaction takes place according to the equation $CdS + I_2 = CdI_2 + S$. The excess of iodine is then titrated with thiosulphate solution and the quantity of cadmium calculated from the amount of iodine consumed. This method yields approximately correct results, but it tends to be untrustworthy, and is not recommended. A better method depends on the reaction between cadmium sulphide and silver nitrate, $CdS + 2AgNO_3 = Ag_2S + Cd(NO_3)_2$. The cadmium sulphide, obtained in the usual way, is collected on a filter and washed with a warm 2% ammonium sulphate solution (to each 250 c.c. of which are added twenty drops of 10% sulphuric acid) until the wash-water no longer gives a reaction with silver nitrate. The filter and precipitate are then transferred to a stoppered cylinder and shaken with 50 c.c. of water and 20 c.c. or more of $N/10$-silver nitrate solution. Five c.c. of 25% nitric acid are now added, the mixture is again shaken for one minute, filtered, and the excess of silver is titrated in an aliquot portion of the filtrate. A similar method may be used for the estimation of zinc. To obtain the zinc sulphide in a condition in which it may be readily filtered and washed, the zinc salt solution is rendered slightly ammoniacal, 2 c.c. of 25% acetic acid are added, the solution treated with hydrogen sulphide, then heated on a water-bath for fifteen minutes, and 1 gram of ammonium sulphate is added. The precipitate is washed with a warm 2% ammonium nitrate solution which has been rendered slightly ammoniacal and then acidified with acetic acid. The method yields from 99·5 to 100·1% of the zinc present. W. P. S.

Colorimetric Method for the Determination of Copper and Iron in Pig Lead, Lead Oxides, and Lead Carbonate. Bernard S. White (*J. Ind. Eng. Chem.*, 1915, **7**, 1035—1036).—From 10—30 grams of material are dissolved in hot nitric acid (1:1), 32 c.c. of sulphuric acid (1:1) are added, and the precipitate washed by decantation, and then on filter-paper. (In the case of red lead, hydrogen peroxide is added after the nitric acid to decompose the lead peroxide). To the filtrate, a slight excess of ammonium hydroxide is added, and the iron estimated colorimetrically in the precipitate by dissolving it in hydrochloric acid and adding a few drops of nitric acid and ammonium thiocyanate solu-

tion. The copper is estimated in the filtrate by adding to the faintly acidified solution six drops of 1:10 potassium ferrocyanide solution, filtering, dissolving the precipitate in ammonium hydroxide rendered faintly acid with hydrochloric acid, and comparing the tint with a standard made by adding the requisite amount of copper sulphate solution to 10 c.c. of ammonium chloride, 2 drops of hydrochloric acid, and 90 c.c. of water. Zinc if present in large amount should be removed by precipitation with sodium ammonium phosphate previous to the copper estimation. G. F. M.

Rapid Volumetric Procedures for Estimating Combined Alumina and Basic Alumina or Free Acid in Aluminium Salts. WILFRED W. SCOTT (*J. Ind. Eng. Chem.*, 1915, **7**, 1059—1061).—The basic alumina or free acid in aluminium salts or technical liquors is estimated by Craig's potassium fluoride method (A., 1911, ii, 335) with minor modifications, such as the addition of 10 c.c. $N/2$-sulphuric acid to the hot aluminium solution before adding the fluoride, and titrating back with $N/2$-potassium hydroxide. Combined alumina is estimated by titration in boiling solution with $N/2$-sodium hydroxide with phenolphthalein as indicator until a pink colour, persistent for at least a minute in the hot solution, is obtained. A correction must be introduced for ferric and ferrous iron, which are nearly always present in technical liquors, since they are likewise dissociated and titrated with the aluminium in the above process. Ferric iron is estimated by titration with stannous chloride before, and total iron after, oxidation with permanganate, and the percentage of $FeO \times 0{\cdot}47 + Fe_2O_3 \times 0{\cdot}64$ is deducted from the aluminium titration. The results obtained show good agreement with gravimetric estimations. G. F. M.

Detection of Iron in Filter Paper which has been Treated with Hydrofluoric Acid. A. GAWALOWSKI (*Zeitsch. anal. Chem.*, 1915, **54**, 547—549).—The traces of iron in filter-paper which has been treated with hydrofluoric acid are usually present in the form of a ferrous-cellulose compound. The iron may be detected by the thiocyanate reaction after the paper has been acidified with dilute hydrochloric acid or sulphuric acid. In this case, the red coloration appears only after the paper, moistened with the acid and reagent, has been exposed to the air for a short time so that the ferrous iron is oxidised. If dilute nitric acid is used in the test, the coloration appears more quickly, but changes gradually to yellow. W. P. S.

Estimation of Oxychloride and of Free Hydrochloric Acid in Solutions of Ferric Chloride. K. FEIST (*Arch. Pharm.*, 1915, **253**, 451—456).—Romyn's method (A., 1915, ii, 489) does not give any information as to the ratio of the iron to the chlorine, and therefore does not show whether, in addition to the acid produced by hydrolysis, any excess of hydrochloric acid is present.

The author therefore recommends, in addition, the estimation of the iron and of the total chlorine by Volhard's method. C. S.

Formic Acid as a Reagent in Essential Oil Analysis. WM. H. SIMMONS (*Analyst*, 1915, **40**, 491—494).—Terpineol is decomposed almost completely by formylation; geraniol and linalool are both converted into an appreciable quantity of ester, whilst santalol is only decomposed slightly. Citronellol, menthol, and the borneol in rosemary oil may be estimated approximately by formylation. The process consists in heating for one hour a mixture of 1 vol. of the oil and 2 vols. of 100% formic acid on a water-bath under a reflux apparatus, washing the esterified oil with saturated sodium chloride solution until free from soluble acid, neutralising it, and estimating the quantity of potassium hydroxide required for its saponification. W. P. S.

Estimation of Reducing Sugars. A Volumetric Method for Estimating Cuprous Oxide without Removal from Fehling's Solution. F. M. SCALES (*J. Biol. Chem.*, 1915, **23**, 81—87).—The cuprous oxide without filtration is converted into cuprous chloride, and then transferred to a known quantity of dilute iodine solution; the iodine which is not reduced is then titrated with sodium thiosulphate. The method gives as accurate results as the gravimetric method, and takes much less time. The method may also be used for the estimation of copper. W. D. H.

Use of Dry Yeast in the Estimation of Sugar in Urine. A. BOLLAND and A. KRAUSZ (*Chem. Zeit.*, 1915, **39**, 947—948).—Dried pressed yeast is preferable to ordinary yeast in the fermentation test for sugars in urine; it may be kept for many months, and does not undergo autofermentation within the period of time required for the test. About 0·5 gram of the dried yeast is mixed with the urine to be tested, and the mixture is filled into an Einhorn's fermentation tube; any sugar present is fermented completely in fifteen to twenty hours at the ordinary temperature. The presence of acetone in the urine does not affect the activity of the yeast. W. P. S.

Microchemical Chitin Reaction. V. VOUK (*Ber. Deut. bot. Ges.*, 1915, **33**, 413—415).—The object is heated for twenty to thirty minutes in a beaker with concentrated, boiling potassium hydroxide solution. The conversion into chitosan is then complete, and the reddish-violet coloration can be obtained in the usual manner. N. H. J. M.

[Estimation of] Benzoyl Peroxide. L. VANINO and F. HERZER (*Arch. Pharm.*, 1915, **253**, 426—440).—The paper gives an account of the methods of preparation, the properties, and the technical, medicinal, and physiological applications of benzoyl peroxide already recorded by various investigators, and contains nothing new except a method of estimation. The peroxide, 0·2—0·3 gram, and

10—15 c.c. of alcohol are heated on the water-bath, an excess of $N/2$-potassium iodide is added, and the mixture faintly acidified. After being heated on the water-bath for four minutes, the mixture is allowed to cool, and is titrated after thirty minutes with thiosulphate solution. The results are accurate. C. S.

Formaldehyde-Fat-Quotient of Milk. G. A. Stutterheim (*Pharm. Weekblad*, 1915, **52**, 1729—1731).—From the results of a great number of analyses, the author draws the conclusion that in good milk the formaldehyde-fat-quotient should not exceed 2·40. A. J. W.

Fat Analysis. I. Soluble and Insoluble Fatty Acids. F. H. Smith (*Chem. News*, 1915, **112**, 319—320).—The saponification number, insoluble and soluble fatty acids, and the mean molecular weight of the insoluble fatty acids may be estimated in one portion of a sample of fat (for example, butter-fat) as follows: Five grams of the fat are saponified by boiling with a definite quantity of alcoholic potassium hydroxide solution, and the excess of alkali is then titrated; the saponification number is calculated from the result. The neutral solution is evaporated to remove alcohol, the residue dissolved in water, and the insoluble fatty acids are liberated by the addition of a slight excess of $N/5$-hydrochloric acid; the mixture is then cooled in ice-water, the liquid portion filtered, and the insoluble fatty acids washed, dried, and weighed. The filtrate is titrated with standard alkali solution and the result, after allowance for the excess of $N/5$-hydrochloric acid added, is expressed in terms of butyric acid or as mg. of potassium hydroxide per gram of fat. The insoluble fatty acids are dissolved in alcohol and the solution titrated to obtain the mean molecular weight of these acids. W. P. S.

Estimation of Water and Fats in Feeding Stuffs. K. Scheringa (*Pharm. Weekblad*, 1915, **52**, 1732—1733).—A description of a simple type of apparatus for estimating moisture and fat in such foods as cheese and cocoa. The extract from the substance is placed in a thick-walled, round-bottomed flask, fitted with a two-hole rubber stopper, and two tubes. One of the tubes is drawn out to a capillary, and air is drawn through the flask by means of a water-pump so as to create a partial vacuum and a continual circulation of air. The flask is heated in a water-bath. A. J. W.

Molecular Weight Estimations of Vegetable Oils. H. J. Backer (*Chem. Weekblad*, 1915, **12**, 1034—1040).—An account of the determination of the density, refractive index, and the iodine and saponification values of certain vegetable oils. The molecular weights have been determined by the cryoscopic method, with benzene as solvent. They have also been calculated from the saponification value (V) from the equation $M = 168000/V$. A. J. W.

Ring Test for Acetone in Urine. C. J. REICHARDT (*Pharm. Zeit.*, 1915, **60**, 765).—Five c.c. of urine are mixed in a test-tube with 2 grams of ammonium chloride and 5 drops of a freshly-prepared sodium nitroprusside solution, and ammonia is poured on the surface of the mixture. If the urine contains more than 0·15 part of acetone per 1000, a violet-coloured zone appears within a few minutes at the junction of the two liquids; with smaller quantities of acetone, a red-coloured zone first appears and changes to violet in about twenty minutes. If the urine is free from acetone, a coloured zone does not develop. W. P. S.

Ammonia and Amino-acids in Urine. W. C. DE GRAAFF (*Pharm. Weekblad*, 1915, **52**, 1777—1781).—An account of estimations of ammonia in urine by Bonnema's method (A., 1915, ii, 648), and a discussion on the presence of amino-acids in urine.
A. J. W.

Estimation of Amino-acids in the Urine. IVAR BANG (*Biochem. Zeitsch.*, 1915, **72**, 101—103).—It is shown that urine can be decolorised in the presence of alcohol by animal charcoal, which, under these conditions, does not remove any of the acids. It can then be employed for the estimation of the amino-acids (+ammonia) by Sörensen's formalin titration method. The urine, before decolorisation, is treated with barium chloride and barium hydroxide. S. B. S.

The Estimation of the Amino-acids of Feeding-stuffs by the Van Slyke Method. II. H. S. GRINDLEY and M. E. SLATER [with H. C. ECKSTEIN and J. C. ROSS] (*J. Amer. Chem. Soc.*, 1915, **37**, 2762—2769).—The lack of concordance between the previous results of the authors and those of Nollau (A., 1915, i, 932) is ascribed to differences in experimental details. The value of the Van Slyke method for the estimation of the chemical groups characteristic of the amino-acids of proteins is again asserted, and it is suggested that the high results obtained by this method for humin nitrogen are due in part to the presence of soluble carbohydrates during the hydrolysis of the proteins and to the presence of cellulose which may mechanically protect some of the protein from complete hydrolysis.

The experimental results published in this paper indicate the existence of marked variations in the free and combined amino-acid content of the common feeding-stuffs, whether referred to the total nitrogen present or to the weight of the feeding-stuff itself. These conclusions are based on experiments with blood meal, tankage, wheat, barley, oats, white soja beans, cottonseed meal, and lucerne hay. D. F. T.

Estimation of Urea in Urine by the Urease Method. CYRUS H. FISKE (*J. Biol. Chem.*, 1915, **23**, 455—458).—The urease method can be made more exact by taking precautions to prevent any escape of ammonia through the acid which receives it.
W. D. H.

Estimation of Alizarin and Certain Other Dyestuffs. EDMUND KNECHT and EVA HIBBERT (*J. Soc. Dyers*, 1915, **31**, 241—244).—For the estimation of alizarin, anthrapurpurin, or flavopurpurin, a weighed quantity of 0·02 to 0·05 gram of the substance is dissolved in 50 c.c. of alcohol, the solution is boiled in a flask into which a current of carbon dioxide is passed, and 10 c.c. of 20% sodium potassium tartrate solution are added, followed by a measured excess of titanous chloride solution. The mixture is again boiled, and the excess of titanous chloride titrated with iron alum solution. All three of the substances show intense blue-green colorations with the excess of titanous chloride; this colour disappears when the last trace of titanous salt has been oxidised by the iron alum. Four atoms of hydrogen are required for the reduction of each of the substances; in the case of alizarin this would correspond with the reduction of the substance to deoxyalizarin. The colouring matters gallocyanin and prune are also quantitatively reduced by titanous chloride, two atoms of hydrogen being required; primuline is not affected by titanous chloride, but primuline-red, formed by diazotising it and combining with β-naphthol, is easily reduced. W. P. S.

Which Constituents of Sour Milk are Precipitated in the Alcohol Test? F. REISS and G. DIESSELHORST (*Bied. Zentr.*, 1915, **44**, 565—567; from *Molk.-Zeit.*, 1915, 742).—The precipitate obtained with 70% alcohol contains the whole of the nitrogen originally present in the milk. Calcium phosphate was found both in the precipitate and filtrate, whilst magnesium phosphate to a great extent remains in solution, although some was found in the precipitate. Two samples of milk were employed, the acidity of which was 11·2 and 29·4 respectively. N. H. J. M.

The Electrometric Estimation of the True Reaction of the Blood. JOSÉ MA. DE CORRAL (*Biochem. Zeitsch.*, 1915, **72**, 1—25).—The author gives a general criticism of the technique of the various methods that have been employed. The results obtained by himself for the hydrion concentration do not differ appreciably from those found by other observers. S. B. S.

The Abderhalden Reaction. DONALD D. VAN SLYKE, MARIAM VINOGRAD-VILLCHUR, and J. R. LOSEE (*J. Biol. Chem.*, 1915, **23**, 377—406).—After incubating serum and substrate, the mixture is freed from protein by colloidal ferric hydroxide, and the free amino-nitrogen is estimated in the concentrated filtrate by the micro-apparatus. The amount of digestive change is estimated by the yield of amino-acid. Every serum, whether from pregnant or non-pregnant individuals, showed protein digestion when incubated with placenta; the range in activity is wide, and the tendency is for pregnant sera to give a somewhat higher result. The differences are too small, however, to make the test decisive even from the quantitative point of view. Carcinoma tissue is digested to about the same extent as placenta. W. D. H.

General and Physical Chemistry.

The Oxy-hydrogen Flame Spectrum of Iron. SIR NORMAN LOCKYER and H. E. GOODSON (*Proc. Roy. Soc.*, 1916, [A], **92**, 260—265).—In continuation of previous work (*ibid.*, 1911, [A], **86**, 78) further observations have been made on the oxy-hydrogen flame spectrum of iron. Sixty-four lines have been identified between λ 3856·52 and λ 5615·88, and of these fifteen have not been previously recorded. These lines are divided into three groups according to the relative strengths in comparison with the lines in an iron arc spectrum. The lines have also been compared with the lines in the electric furnace spectrum and with the solar and stellar lines of iron. H. M. D.

Kinetics of the Multirotation of Gelatin Sols. WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1915, **17**, 113—119).—From observations made by Trunkel (A., 1910, i, 648) on the change in the optical rotatory power of gelatin sols with time, it is shown that the observed rotation $[\alpha_t]$ changes with the time t according to the equation $[\alpha_t]_D = k \cdot t^{0 \cdot 06}$. The coefficient k is a linear function of the concentration c and of the temperature θ, as represented by the equations: $k = 0{\cdot}687(100c + 186)$ and $k = 9{\cdot}17(38 - \theta)$. The range covered by the experimental observations from which these formulæ are derived is indicated by the following limiting values: $c = 0{\cdot}25$ to $0{\cdot}76\%$, $\theta = 15°$ to $25°$, and $[\alpha]_D = -112°$ to $-245°$.

The kinetic investigation of other properties of gelatin sols has not yet been sufficiently investigated to say whether similar relations obtain in the case of the viscosity, surface tension, and other properties. H. M. D.

The Existence of a Compound of Polonium and Hydrogen. ROBERT W. LAWSON (*Monatsh.*, 1915, **36**, 845—852).—In the course of a determination of the range of the α-particles emitted by polonium in an atmosphere of hydrogen, it was found that the ionisation current at a given distance from the source of rays gradually increases with time. In explanation of this effect it is suggested that a volatile compound is formed by the combination of polonium and hydrogen. This compound is rapidly decomposed by ionised oxygen. The analogy of polonium to the elements of the sulphur group is quite consistent with the theory put forward. H. M. D.

Distribution of Solvents between Solutes. IV. Electrical Conductivity of Mixtures of Acids. A. G. DOROSCHEVSKI and V. I. FRIDMAN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1615—1626. Compare A., 1914, ii, 610).—The observed conductivities of mixed solutions of hydrochloric and nitric acids are in agreement with the values calculated on the assumption of isohydry at equivalent

concentrations, the water in these solutions being, therefore, distributed between the solutes in proportion to their chemical masses; Wakeman's calculations of the conductivities of mixtures of acetic acid with various other acids (A., 1895, ii, 68) are shown to be erroneous to some extent. Calculation of Barmwater's results (A., 1904, ii, 10) shows that mixed aliphatic acids in dilute solution obey the above law, and the same is shown by the authors' measurements to be the case with mixtures of acetic, propionic, and butyric acids in comparatively high concentrations (5—10%). T. H. P.

A Study of Double Salts in Standard Cells. G. F. LIPSCOMB and G. A. HULETT (*J. Physical Chem.*, 1916, **20**, 75—82).—With a view to the application of double salts of zinc in the construction of cells suitable as standards of electromotive force, the authors have investigated the equilibrium relationships in the ternary systems potassium sulphate, zinc sulphate, water, and potassium chloride, zinc chloride, water at 25°.

Cells of the type Zn amalgam|S||Hg_2SO_4|Hg, in which S represents a solution saturated with respect to (1) the double salt $K_2SO_4,ZnSO_4,6H_2O$, (2) the double salt and K_2SO_4, and (3) the double salt and $ZnSO_4,7H_2O$, were examined, with the result that the third cell only was found to give constant results. Its *E.M.F.* is 1·41976 at 25° and the temperature-coefficient is −0·00133.

The cell Cd amalgam|S||Hg_2Cl_2|Hg, in which S represents a saturated solution of the double salt $2KCl,CrCl_2,6H_2O$, was also found to give accurately reproducible and constant results. Its *E.M.F.* at 25° is 0·70505 and the temperature-coefficient +0·00015. The corresponding zinc cell has an *E.M.F.*=1·01857 at 25°, but hydrolysis appears to take place slowly. H. M. D.

Electromotive Forces. WILDER D. BANCROFT (*J. Physical Chem.*, 1916, **20**, 64—74).—A plea for consistency in the derivation of the formulæ for the *E.M.F.* of concentration cells of different types. It is shown that the formula for the reaction isotherm $E=RT/nF \cdot \log k\Sigma p_1/\Sigma p_2$ may be applied in the derivation of the *E.M.F.*'s of all such cells. H. M. D.

The Periodic Passivity of Iron. A. SMITS and C A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 807—811). —Previous observations have shown that passive iron is rendered active under the influence of chlorine, bromine, and iodine ions which act as catalysts. The passive condition may be produced by anodic polarisation in suitable circumstances, and according to Smits this is due to the disturbance of the equilibrium between the active and passive forms in the surface layers of the metal in consequence of the dissolution of the active (ferrous) modification. Halogen ions and anodic polarisation thus tend to produce opposite effects, and when an iron anode immersed in a solution of ferrous sulphate, to which chlorine ions have been added in suitable concentration, is subjected to the influence of a current, it is found that well-developed periodic phenomena are observed. The requisite

concentration of the chlorine ions depends on the current density, and the relative lengths of the active and passive periods can be varied by suitable adjustment of these factors. The oscillations in the electrode potential amount to 1·74 volts, and in the particular experiment which the authors describe, the lengths of the two periods were each approximately equal to six seconds. H. M. D.

Transport Numbers in Non-aqueous Solutions. A. N. SACHANOV and A. M. GRINBAUM (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1769—1789).—The authors have measured at the ordinary temperature (about 18°) the transport numbers for silver nitrate in aniline (dielectric constant, 6·85) and mixtures of aniline with pyridine containing (1) 80 vol. % of the former (8·0), and (2) 50 vol. % (9·7). The results obtained, together with those of Schlundt (A., 1902, ii, 492) for solutions of silver nitrate in pyridine (12·56) and in acetonitrile (35·8) and those of Hittorf for solutions in water (81·0) give a complete view of the variation of the transport numbers for this salt with the concentration and with the dielectric constant of the solvent (compare Sachanov and Prsheborovski, A., 1915, ii, 729; Sachanov and Rabinovitsch, A., 1915, ii, 730).

In the aniline–pyridine mixtures and also in pyridine and acetonitrile, the transport number for silver diminishes as the concentration increases. For one and the same concentration the transport number diminishes with diminution of the dielectric constant of the solvent. In aniline, on the other hand, the transport number increases as the concentration increases from $V=5$ to $V=1$. These results are explained on the assumption of the formation of complex anions, $Ag(NO_3)_2'$, and complex cations, $(AgNO_3)^{\cdot}$. T. H. P.

Magneto-chemistry: Applications to Analytical Chemistry. A. QUARTAROLI (*Gazzetta*, 1915, **45**, ii, 406—423).—Even in moderately concentrated solutions, ordinary salts, such as those of the alkali and alkaline-earth metals, aluminium, ammonium, etc., which are diamagnetic, exhibit in general susceptibilities differing little from that of water. Further, the difference in susceptibility between concentrated solutions of magnetic salts and water is some hundreds of times as great as that between concentrated solutions of diamagnetic salts and water. In order to be able to utilise magnetochemical data in quantitative analysis, the author employs a method based on the fact that water is diamagnetic, and that there exists for each magnetic salt a concentration at which its aqueous solution is magnetically inactive. For the measurement of these concentrations the use of Quincke's manometer is tedious and the author employs an apparatus based on the fact that a current of air-bubbles escaping from a capillary tube dipping below the surface of a magnetic solution situate between the poles of an electromagnet is retarded when the magnet is excited; on the other hand, *no retardation or acceleration occurs with a liquid which is inactive* or, more accurately, has a susceptibility equal to that of air. The apparatus, which is readily fitted up, is depicted and the method

of using it described. The accuracy attainable is shown by the fact that a distinction is readily made between manganous chloride solutions containing 2·59 grams (inactive) and 2·57 grams of manganese per litre; still greater accuracy would result from the use of a magnetic field of more than 25,000 gauss, which was about the value employed by the author.

These critical concentrations have been determined for a number of ferric, ferrous, manganous, cobalt, nickel, and copper salts. The influence of the anion is negligible, excepting in the case of the sulphates, and, unless they are present in very large excess, the ordinary diamagnetic salts or mineral acids produce only small alterations in the inactive concentration of the magnetic salt.

In determining the concentration of a salt of a magnetic metal in solution, the latter is either diluted with water or concentrated by evaporation or addition of a stronger solution of the salt, until it becomes magnetically inactive. From the known degree of the dilution or concentration necessary, the initial concentration may be calculated. Where other metals are also present, the method may often be used in conjunction with ordinary analytical methods. Its use in this way is described for the estimation of: (1) chromium, iron, or manganese in presence of aluminium; (2) iron and chromium together; (3) iron, manganese, aluminium, and phosphate; (4) chromium and manganese; (5) nickel and cobalt.

T. H. P.

The Physical Properties of Metals as Functions of Each Other. A. H. STUART (*J. Inst. Metals*, 1915, **14**, 168—177).—When the atomic heats of those metals which obey the law of Dulong and Petit are tabulated, the values are found to lie between 5·93 and 6·67. Deviations not exceeding 2% of the observed specific heat may be attributed to experimental error, and when the deviations from the law which exceed this are plotted against the atomic weights, the points are found to lie on two smooth curves, corresponding with positive and negative errors respectively. These curves of deviation are closely represented by the formulæ:

$$xy^{1\cdot02}=0\cdot285 \quad \text{and} \quad xy^{0\cdot64}=2\cdot2.$$

A relation of the following form is also found: Atomic weight = 1·41 × density ÷ product of coefficient of elasticity and coefficient of linear expansion.

C. H. D.

Apparatus for Determining Melting-points at Temperatures above 270°. P. RASSFELD (*J. pr. Chem.*, 1916, [ii], **92**, 467—468). —The apparatus consists essentially of an inverted T-tube, the horizontal limb of which passes through opposite sides of a small metal (tin) bath. The thermometer and capillary tube are adjusted in the vertical limb, so that the substance can be seen by looking through the horizontal tube against a light. Such a bath can be quickly heated, but is not influenced by draughts, and therefore has advantages over the Maquenne block or Thiele's copper block.

J. C. W.

The Measurement of Very Low Temperatures. XXVI. The Vapour Pressures of Oxygen and Nitrogen According to the Pressure Measurements by von Siemens and the Temperature Determinations by Kamerlingh Onnes. G. HOLST (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 829—839).—A recalibration of the platinum resistance thermometer which was used by von Siemens (A., 1913, ii, 1023) in the determination of the temperature in measurements of the vapour pressures of liquid oxygen and nitrogen has revealed small errors in the thermometer readings The results obtained are employed to correct the vapour-pressure tables given by von Siemens. H. M. D.

A Thermostat for Moderate and High Temperatures JOHN L. HAUGHTON and D. HANSON (*J. Inst. Metals*, 1915, **14**, 145—153). —A glass or silica bulb containing air is inserted in the furnace and connected with a capillary tube containing mercury. A U-tube encloses a mercury switch, by means of which a small current, actuating a relay which controls the heating current, is regulated. Variations of atmospheric pressure are compensated for by a second bulb of similar size on the other side of the U-tube, cooled by ice. The principal difficulty of such a control arises from the lag of the air vessel behind the temperature of the furnace. To overcome this difficulty the bulb is made of annular form, the specimen to be kept at constant temperature being placed in the inner space, so that the lag reduces the fluctuations of temperature. At 400° the fluctuations do not exceed 1°. For higher temperatures the bulb should be of silica. C. H. D.

History of Specific Gravity. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1915, **39**, 985—986. Compare *ibid.*, 1912, **36**, 385, 629, 1201; this vol., ii, 84).—A reply to H. Schelenz; this writer does not seem to be aware of previous publications by the author. W. P. S.

Binary Mixtures. I. The Densities and Viscosities of Mixtures containing Phenol. ARTHUR BRAMLEY (T., 1916, **109**, 10—45).—In order to ascertain the factors which influence the viscosity of liquid mixtures and the possibility of determining the composition of any compound which may be formed, measurements have been made of the densities and viscosities of mixtures of phenol with bases of varying strength over a wide range of temperature. For comparative purposes, the viscosity-composition curves given by phenol in admixture with benzene, chlorobenzene, and nitrobenzene, which may be regarded as indifferent substances, were also determined. These curves show a very marked curvature and are convex towards the axis of composition. This behaviour is probably connected with the gradual breaking down of the associated phenol molecules.

The curves for the mixtures with aniline, *p*-toluidine, and quinoline show a maximum which becomes less clearly marked as the temperature is increased. That the character of these curves is determined by the acidic nature of phenol is shown clearly by

comparison of the curves with that for mixtures of phenetole and aniline. This is convex towards the axis of composition. The position of the maximum varies with the temperature, and, furthermore, for all the mixtures examined, it is found that the composition of the mixture, for which the deviation from the requirements of the mixture rule has a maximum value, depends on the temperature. When curves are drawn to show the relation between the composition of the maximum deviation mixture and the temperature, it is found that these are all convex towards the axis of composition. A further characteristic is that they lie entirely on one side of the ordinate which corresponds with equimolecular proportions of the components, and if produced in the direction of higher temperatures they appear to approach this ordinate asymptotically. It is supposed that these peculiarities are the result of unequal thermal dissociation of the molecular complexes of phenol and of the compound formed, rise of temperature being favourable to the dominating influence of the compound.

Mixtures of phenol with pyridine give sinuous curves which show a positive maximum at higher temperatures only. The curves for the mixtures with dimethylaniline, diphenylamine, and diphenylmethylamine show no maximum, and this is in agreement with the weaker basic nature of these substances, the effect of compound formation being to a large extent counterbalanced by the effect of the dissociation of the molecular complexes of phenol.

The curves for mixtures of phenol and acetone are convex towards the axis of composition, and although evidence has been adduced in favour of the formation of a compound in this case, it would seem that the influence of the dissociation of the complex phenol molecules is predominant in determining the nature of the curves.

The density-composition curves deviate in most cases only slightly from the mixture rule line. Considerable deviations are found, however, in the case of the pyridine mixture, the maximum deviation occurring at 59—60% of phenol whatever the temperature. Still greater deviations are shown by the quinoline mixtures, the density curves for which show a maximum. The maximum deviation from the mixture rule line occurs at 47% of phenol, and this composition remains unchanged when the temperature is altered. From a comparison of the viscosity and density curves it is evident that increase in density is not the dominant factor in determining increase in viscosity. H. M. D.

The Temperature-coefficients of the Free Molecular Surface Energy of Liquids from − 80° to 1650°. XIII. The Surface Energy of Position-isomeric Benzene Derivatives. F. M. JAEGER and JUL. KAHN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 595—616. Compare A., 1915, ii, 747, 748).—The results of the investigation of the surface tension of some thirty-six position isomerides are given in the following summary, which shows the temperature-coefficients of the molecular surface energy and the equations for the change of density with temperature. Where the

temperature-coefficient changes appreciably with the temperature, the limiting values are given, the first value having reference to the lowest range of temperature: *o*-Dinitrobenzene, 1·95, $D=1·3349-0·001215(t-100)+0·0^5325(t-100)^2$; *m*-dinitrobenzene, 2·05–1·71, $D=1·3557-0·00106(t-100)-0·0^51(t-100)^2$; *p*-dinitrobenzene, 1·35; *m*-fluoronitrobenzene, 1·82, $D=1·3484-0·001202t+0·0^688t^2$; *p*-fluoronitrobenzene, 2·09, $D=1·3509-0·0010275t-0·0^678t^2$; *o*-chloronitrobenzene, 2·16, $D=1·3866-0·001014t-0·0^64t^2$; *m*-chloronitrobenzene, 2·19, $D=1·3788-0·00086t-0·0^5112t^2$; *p*-chloronitrobenzene, 1·88, $D=1·3285-0·00117(t-60)+0·0^688(t-60)^2$; *p*-dichlorobenzene, 1·83, $D=1·2531-0·001064(t-50)-0·0^664(t-50)^2$; 1:2-dichloro-4-nitrobenzene, 1·96, $D=1·5464-0·001238t+0·0^64t^2$; 1:3-dichloro-4-nitrobenzene, 2·16, $D=1·5241-0·001028t-0·0^664t^2$; 1:4-dichloro-2-nitrobenzene, 2·01, $D=1·5194-0·001012t-0·0^68t^2$; *o*-bromonitrobenzene, 2·19, $D=1·6642-0·001228(t-50)-0·0^632(t-50)^2$; *m*-bromonitrobenzene, 2·04, $D=1·6625-0·001166(t-50)-0·0^672(t-50)^2$; *p*-bromonitrobenzene, 1·87; *o*-iodonitrobenzene, 1·98, $D=1·9541-0·001422(t-50)$; *m*-iodonitrobenzene, 2·16, $D=1·9816-0·001342(t-25)-0·0^656(t-25)^2$; *p*-nitrotoluene, 1·77–2·30, $D=1·1239-0·000764(t-50)-0·0^516(t-50)^2$; *o*-nitrophenol, 1·35–3·20, $D=1·2832-0·000974(t-50)-0·0^688(t-50)^2$; *m*-nitrophenol, 0·50–3·1, $D=1·2797-0·000716(t-100)-0·0^516(t-100)^2$; *p*-nitrophenol, 1·81, $D=1·2874-0·000855(t-100)$; *p*-nitroanisole, 1·49–2·80, $D=1·2246-0·00093(t-50)-0·0^624(t-50)^2$; *o*-cresol, 1·92, $D=1·0693-0·000966t+0·0^5104t^2$; *p*-cresol, 1·80, $D=1·0526-0·000888t+0·0^68t^2$; *o*-chloroaniline, 1·97–1·1, $D=1·2388-0·001047t+0·0^51t^2$; *p*-chloroaniline, 1·98–1·24, $D=1·2337-0·000903t$; *m*-nitroaniline, 1·74, $D=1·2269-0·00087(t-100)$; *p*-nitroaniline, 1·3; 3-nitro-*o*-toluidine, 1·27–1·9, $D=1·1900-0·0008815(t-100)$; 5-nitro-*o*-toluidine, 4·2; 3-nitro-*p*-toluidine, 3·08, $D=1·1821-0·000882(t-100)$; sylvestrene, 2·28–3·9, $D=0·8779-0·0007t-0·0^68t^2$; terebene, 2·16, $D=0·8932-0·000846t$.

The results obtained show that the molecular surface energies of position isomerides at one and the same temperature are not in general equal, although this would seem to be suggested by certain earlier observations. The energy-temperature curves of halogen- or nitro-substituted aromatic compounds are frequently very similar, but great differences are found in the behaviour of the isomeric nitro-phenols. The corresponding anisoles show much smaller differences, and it is supposed that the anomalous behaviour of the nitrophenols relatively to one another is connected with structural differences other than those corresponding with ordinary position isomerism. These differences, to which attention has been frequently directed, are thus clearly reflected in the energy-temperature curves.

Within the group of the halogen-substituted nitrobenzene derivatives, as in the halogen derivatives of benzene, the molecular surface energy at a given temperature increases with increasing atomic weight of the halogen. H. M. D.

The Temperature-coefficients of the Free Molecular Surface Energy of Liquids from $-80°$ to $1650°$. XIV. Measurements of a Series of Aromatic and Heterocyclic Substances. F. M. JAEGER and JUL. KAHN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 617—635).—The results obtained for the twenty-eight compounds examined are summarised as in the preceding abstract: 1 : 2 : 4-chlorodinitrobenzene, 2·23, $D=1·5267-0·001158(t-50)+0·0^67(t-50)^2$; *p*-dibromobenzene, 2·15, $D=1·8649-0·0016475(t-80)-0·0^6625(t-80)^2$; iodobenzene, 1·65–2·80, $D=1·8606-0·0015t-0·0^616t^2$; *o*-bromotoluene, 2·09, $D=1·4470-0·00119t$; phenol, 1·36–1·94, $D=1·1097-0·001208t+0·0^5144t^2$; 2 : 4-dinitrophenol, 1·90, $D=1·4507-0·000962(t-100)-0·0^662(t-100)^2$; 2 : 4 : 6-trichlorophenol, 1·57–3·02, $D=1·5236-0·001382(t-50)-0·0^5168(t-50)^2$; *p*-nitrophenetole, 2·0, $D=1·1656-0·00096(t-50)$; 2-nitroresorcinol; veratrole, 3·47–1·66, $D=1·1051-0·00095t-0·0^624t^2$; 4 : 5-dinitroveratrole, 2·32–5·5, $D=1·3374-0·001035(t-120)-0·0^675(t-120)^2$; ethyl cinnamate, 2·41, $D=1·0687-0·000934t+0·0^656t^2$; anisaldehyde, 2·06, $D=1·1421-0·000894t+0·0^624t^2$; benzophenone, 2·27, $D=1·1064-0·00077(t-25)-0·0^64(t-25)^2$; 3 : 4 : 3′ : 4′-tetrachlorobenzophenone; 2 : 4 : 2′ : 4′-tetrachlorobenzophenone dichloride, 1·21 – 2·32, $D=1·4570-0·0009425(t-140)$; methylaniline, 1·90, $D=1·0146-0·001004t+0·0^648t^2$; *p*-nitromethylaniline, 1·3–3·3, $D=1·2049-0·0008125(t-150)$; nitrosomethylaniline, 1·63–2·27, $D=1·1430-0·000868t$; di*iso*butylaniline, 3·43–2·73, $D=0·9319-0·000924t+0·0^5176t^2$; diphenylamine, 2·31, $D=1·0628-0·000892(t-50)+0·0^5112(t-50)^2$; dibenzylamine, 2·53, $D=1·045-0·00082t$; azoxybenzene, 1·53–4·98, $D=1·1764-0·000782t$; α-dihydrocampholenic acid; ethyl α-dihydrocampholenate, 2·46, $D=0·9445-0·0008t$; furfuraldehyde, 2·70, $D=1·1851-0·001176t+0·0^696t^2$; thiophen, 1·90, $D=1·0873-0·001224t+0·0^696t^2$; piperidine, 1·98, $D=0·8821-0·00092t$.

These data are discussed with reference to the influence of substitution on the molecular surface energy at constant temperature. As a general rule, it would seem that this energy increases when the hydrogen atom is replaced by the halogens, the nitro-group, and by hydrocarbon radicles. H. M. D.

The Adsorption of Sodium Hydroxide by Cellulose. ALAN LEIGHTON (*J. Physical Chem.*, 1916, **20**, 32—50).—Previous experiments on the adsorption of sodium hydroxide by cellulose have led to contradictory conclusions, and the present series was designed to throw further light on the nature of the mercerising process.

The experiments were made with a "normal" cellulose prepared by heating best grade absorbent cotton for eighteen hours at 100° in a solution containing 20 grams of sodium hydroxide per litre. After this treatment, the cotton was washed with water, then with dilute hydrochloric acid, and again with water until neutral. It was then washed with alcohol and ether and died at 115°.

The "normal" cellulose was submitted to the action of sodium hydroxide solutions of varying concentration for three hours. By

centrifuging the mercerised cotton for an hour at about 4000 revolutions per minute, it was found possible to remove almost completely the adhering liquid. The cotton and the residual solution were then analysed.

The results obtained show that the quantity of sodium hydroxide taken up by 1 gram of cellulose is a continuous function of the concentration of the solution. There is no evidence whatever to justify the assumption that a definite chemical compound is formed. The actual quantity of sodium hydroxide adsorbed per gram of cotton increases from 0·1 gram in a solution containing 25 grams per litre to 0 92 gram in a solution containing 475 grams per litre. The quantity of adsorbed water remains constant until the adsorbed sodium hydroxide reaches about 0·34 gram per gram of cotton, but for larger quantities of the hydroxide the amount of adsorbed water gradually decreases from 4·0 grams to 0·82 gram. The former value corresponds with solutions which contain less than about 100 grams of sodium hydroxide per litre, and the latter with a solution containing 475 grams per litre. H. M. D.

The Preparation of Collodion Membranes of Different Permeability. William Brown (*Biochem. J.*, 1915, **9**, 591—617).—Collodion thimbles of regularly increasing degree of permeability may be prepared by soaking air-dried thimbles in alcohol–water mixtures of increasing alcohol content. The diffusive capacity of any substance through collodion may be specified in terms of the alcohol strength required to produce the membrane which just prevents its passage. This may be termed the "alcohol index" of the substance. W. D. H.

The Laws of Solution. Henry Le Chatelier (*Compt rend.*, 1916, **162**, 29—32).—Polemical. A reply to Colson (compare this vol., ii, 15). W. G.

The Irrational Character of the Formulæ of Solubility and Heats of Wetting. Albert Colson (*Compt. rend.*, 1916, **162**, 222—224).—A reply to Le Chatelier (preceding abstract). W. G.

Hydrates in Solution. Gertrud Kornfeld (*Monatsh.*, 1915, **36**, 865—897).—The properties of aqueous solutions of pyridine seem to show that combination takes place between the two substances, but the question is by no means settled. In the further investigation of the behaviour of these substances towards one another, freezing-point measurements have been made for a number of solutions obtained by the addition of measured quantities of pyridine and water to the same solvent. The freezing-point data show that no measurable combination occurs in aniline, but that this takes place to a small extent in urethane and formamide and to a relatively large extent in ethylene dibromide. The compound thus indicated has the formula $2C_5H_5N,H_2O$.

From the freezing-point curve for pure aqueous solutions of

pyridine, according to which the molecular weight of the pyridine gradually increases from 82 in a 1% solution to 148 in a 17% solution, the conclusion is drawn that the compound $6C_5H_5N,H_2O$ is present in the more concentrated solutions.

The behaviour of copper sulphate, ferric chloride, sodium sulphate, and calcium chloride in formamide solutions and the effect of the addition of water have also been examined by freezing-point measurements. These are also considered to furnish evidence in support of the view that salt hydrates are formed. H. M. D.

Growth of Crystal Polyhedra in their Fusions. R. NACKEN (*Jahrb. Min.*, 1915, ii, 133—164).—Experiments were made on the rate of growth of single crystals of salol (m. p. 41·7°) and benzophenone (m. p. 47·7°) in small tubes filled with the fused material and kept at the melting-point temperature in a water-bath. The crystal was supported on a copper rod which was maintained at a slightly lower temperature, the heat of crystallisation being thereby conducted away. Within certain limits the rate of crystallisation is proportional to this temperature difference, but with under-cooling it is increased, and the curves show a maximum. L. J. S.

Metallic Crystal Twinning by Direct Mechanical Strain. C. A. EDWARDS (*J. Inst. Metals*, 1915, **14**, 116—144. Compare Timoféev, A., 1912, ii, 1054).—That twinning may be produced directly in metals by mechanical strain, without subsequent annealing, is proved by experiments with tin, twinning being practically absent when the temperature during straining is 100°, whilst numerous twins are produced at low temperatures, even when the metal is strained in liquid air. Zinc behaves in a similar manner. Evidence is also given for the view that twinning results in an increase of hardness (A., 1915, ii, 565). C. H. D.

The Theory of Emulsification. WILDER D. BANCROFT (*J. Physical Chem.*, 1916, **20**, 1—31. Compare A., 1915, ii, 530).—A general discussion of phenomena which are supposed to afford evidence in support of the view that gases and vapours are selectively adsorbed by all solids and liquids. This adsorption is said to be a source of error in the determination of the molecular weights of substances in solution by air-bubbling methods. The change of the surface tension of mercury with time cannot, however, be satisfactorily explained in terms of the gas adsorption at the mercury surface. H. M. D.

The Emulsifying Action of Soap. A Contribution to the Theory of Detergent Action. S. A. SHORTER and S ELLINGWORTH (*Proc. Roy. Soc.*, 1916, [A], **92**, 231—247).—Recent work on emulsification has shown that saponification plays no part in the emulsification of oils by alkali, and that the lowering of the interfacial tension and the emulsification depend on the presence of free fatty acid in the oil. In further investigation of the nature of detergent action, measurements have been made, by a stalagmometric method,

of the influence of potassium hydroxide, and of potassium oleate in presence of excess of alkali and of oleic acid, on the surface tension of water against pure benzene and benzene containing small quantities of oleic acid (acidified benzene).

If n and n_a are the drop numbers of pure water against pure and acidified benzene respectively, N and N_a the corresponding values for a soap solution, then it may be assumed that the effect of the undecomposed soap is to change the acidified benzene drop number from n_a to Nn_a/n, that is to say, in the ratio N/n. The effect of the alkali is then represented by a change in the drop number from Nn_a/n to N_a. The ratio of these numbers, $N_a n/Nn_a$, affords a measure of the surface activity of the alkali. The actual magnitude of the surface activity will, of course, be measured by the logarithm of this ratio, and hence the ratio of the surface activity of the alkali to that of the soap will be given by $\log (N_a n/Nn_a)/\log N/n$.

In terms of the above ratios it is found that towards acidified benzene the surface activity of the alkali produced by hydrolysis is much smaller than that of the undecomposed soap; further, that the surface activity of the free alkali in a soap solution is less than that of the same quantity of alkali in pure water, and that the addition of alkali to a soap solution increases the surface activity of the soap. The last-mentioned effect is much too large to be explained by the suppression of hydrolysis. In explanation of the phenomenon it is suggested that the alkali exerts a coagulating influence on the soap, the result of which is an increase in the average size of the semi-colloidal particles, and hence an increase in the "surface activity" of the soap. In reference to the nature of this coagulating influence, it is pointed out that other electrolytes, such as potassium and sodium chlorides, also increase the "surface activity" of the soap, but the effect of salts is much smaller than that of alkali. H. M. D.

The Influence of Capillary-active Substances on the Stability of an Arsenic Trisulphide Sol. C. F. van Duin (*Kolloid Zeitsch.*, 1915, **17**, 123—130. Compare Kruyt and van Duin, A., 1914, ii, 182).—In continuation of previous experiments on the influence of organic substances on the coagulation of colloidal arsenious sulphide by electrolytes, observations have been made with pure *iso*butyl alcohol. The adsorption of the alcohol from aqueous solution by charcoal was also examined, the changes in concentration being determined stalagmometrically. By comparison of the results with those previously obtained for phenol and *iso*amyl alcohol, it is found that the influence of the three substances on the coagulating concentration of electrolytes runs parallel with the absorbability of the three substances by animal charcoal.

Further experiments, in which adsorption measurements were made, on the one hand with chemically pure substances, and on the other with commercial samples, have shown that impurities have no appreciable influence on the adsorption of *iso*butyl alcohol, whereas the adsorption curves for phenol and *iso*amyl alcohol vary markedly with the degree of purity of the substances. This varia-

tion is suggested as the basis of a method for the examination of the purity of phenol and *iso*amyl alcohol.

The method employed in the preparation of pure *iso*butyl alcohol depends on the formation of an *iso*butyl ether of trinitrophenylmethylnitroamine when ordinary *iso*butyl alcohol (b. p. 105—110°) is allowed to react with tetranitrophenylmethylamine on the water-bath. The excess of *iso*butyl alcohol and the *iso*butyl nitrite formed are distilled off and the ether repeatedly crystallised from ethyl alcohol until colourless. M. p. 95°. The ether is then decomposed by ammonia, whereby *iso*butyl alcohol is set free. The solution is acidified with sulphuric acid, filtered, and the filtrate subjected to distillation in steam. This is followed by treatment with potassium carbonate and metallic calcium. The pure substance has b. p. 108—108·2° at 771 mm. H. M. D.

Forms of Distribution of Metallic Silver. R. ED. LIESEGANG (*Kolloid Zeitsch.*, 1915, **17**, 141—145).—As the result of earlier experiments on the interaction between substances which diffuse towards one another in a gelatinous medium, the view has been expressed that the growth of precipitates is limited to one side of the initial precipitation film. This is shown not to be the case in the interaction of silver nitrate and quinol.

Other experiments on the reaction of silver nitrate with ferrous sulphate and with ferrous chloride by diffusion in a gelatin medium show that the structure and mode of distribution of the resulting silver depend on the concentration of the ferrous salt solution. H. M. D.

The Adsorption Capacity of Living Yeast. PAUL ROHLAND and FRANZ HEYDER (*Kolloid Zeitsch.*, 1915, **17**, 139—141).—Comparative observations on the adsorption of various dyes by colloidal silicates, animal charcoal, and yeast show that there is a certain parallelism in the behaviour of these adsorbents. H. M. D.

Invariant, Univariant, and Bivariant Equilibria. III. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 820—828. Compare A., 1915, ii, 619).—A discussion of the types of equilibrium in quaternary systems. H. M. D.

The Equilibrium Liquid-vapour of the System Argon–Nitrogen. G. HOLST and L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 872—894).—Measurements have been made in order to obtain the relations between the pressure, temperature, and composition in the condensation of mixtures of nitrogen and argon. From the experimental data diagrams have been constructed showing the connexion between the composition of the co-existing phases and the temperature at different pressures, and between the pressure and the composition at constant temperature. The ratio, r', of the components in the liquid phase is connected with the corresponding ratio r for the vapour phase by the equation $\log r' = a + b \log r$, where a and b are constants. Since r and r' do not differ very

much, it is to be expected that argon and nitrogen will not be easily separated by any process of fractional condensation or distillation.

For gaseous mixtures the change in pv with varying pressure can be represented, with an error of less than 0·1%, by the equation $pv = RT(1 + B/v)$, in which B is a constant which depends on the composition of the mixture.

New measurements of the vapour pressures of liquid oxygen, nitrogen, and argon are recorded, and a redetermination of the temperature and pressure at the triple point for argon has given $T = 83·81°$ (abs.) and $p = 521·4$ mm.

A method for the estimation of the composition of mixtures of argon and nitrogen is described which depends on the absorption of the nitrogen when subjected to the action of the glow discharge through potassium vapour. The results obtained by this method are in agreement with those derived from density measurements, provided that the value recently obtained by Schultze (A., 1915, ii, 833) for the density of pure argon is used in the calculations.

H. M. D.

Critical End-points in Ternary Systems. III. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 793—807).—A theoretical paper dealing with special cases of equilibrium in ternary systems. H. M. D.

The Propagation of Flame in Mixtures of Hydrogen and Air. The "Uniform Movement." WILLIAM ARTHUR HAWARD and TATSURO OTAGAWA (T., 1916, **109**, 83—89).—The phenomena which precede the development of the explosion wave in mixtures of hydrogen and air resemble closely those which have been observed for mixtures of methane and air. When a mixture is ignited at the open end of a horizontal tube, closed at the other end, a "uniform movement" of the flame is set up, which has been examined with reference to its dependence on the composition of the gas mixture and the diameter of the tube.

According to Mallard and Le Chatelier, maximum speed is obtained with a mixture containing 40% of hydrogen, but the authors' results show that the maximum extends over the range 38—45% of hydrogen. For mixtures containing up to 35% of hydrogen the speeds in a 11·5 mm. tube are greater than in a 9 mm. tube, whilst in a 25 mm. tube the speeds for mixtures containing up to 54% of hydrogen are considerably greater than those obtained in tubes of 9 and 11·5 mm. diameter. On the other hand, the velocities of the uniform movement in mixtures containing more than 54% of hydrogen are almost identical in the three tubes. According to these results, it would seem that the cooling effect produced by the walls of the tubes becomes inappreciable when the thermal conductivity of the gaseous mixture is high. In this connexion it is to be noted that the thermal conductivity of hydrogen is about six times as large as that of air. H. M. D.

Influence of Pressure on the Combustion of Explosive Gas-Air Mixtures. E. TERRES and F. PLENZ (*Chem. Zentr.*, 1915, ii, 1278—1279; from *J. Gasbeleucht.*, 1914, **57**, 990—995, 1001—1007, 1016—1019. Compare *ibid.*, 1914, **57**, 893).—The influence of pressure on the explosive limits of mixtures of hydrogen, carbon monoxide, and methane with air, and on the processes of combustion has been investigated by estimations of the products of the reactions. Increase of the initial pressure restricts the region of explosion, particularly with the mixtures containing carbon monoxide; the upper limit of explosion of methane furnishes, however, an exception to this rule. The explosion limit is by no means a sharply defined region, diminishing concentration leading gradually from the region of explosion through one of decreasing partial combustions to mixtures which do not ignite. With hydrogen and methane, such partial combustions are lacking at the upper limit of explosion. The explosive limits are defined as the concentrations of combustible gas at which the heat developed in unit time exactly covers the loss, so the combustion either just does or just does not proceed through the mixture. With rise of temperature these limits are extended. As regards the ignition it is found that no essential difference exists between ignition by heating and ignition by a spark; the locality of the ignition does, however, exert a marked influence on the value of the partial combustions. T. H. P.

The Velocity of Ionic Reactions. GERTRUD KORNFELD (*Monatsh.*, 1915, **36**, 941—943).—On the assumption that the neutralisation of weak bases by weak acids might require a measurable time for completion, conductivity measurements have been made according to the method described by Benedicks (A., 1910, ii, 280) to determine the time required for the neutralisation of $N/10$-solutions of phenol and pyridine. These show that the process is complete in less than 1/250th of a second. H. M. D.

Studies in Catalysis. III. Preliminary Measurements of the Infra-red Absorption Spectra of Hydrogen Chloride, Potassium Chloride, and Methyl Acetate in Aqueous Solution. RAPHAEL HEBER CALLOW, WILLIAM CUDMORE MCCULLAGH LEWIS, and GERALD NODDER (T., 1916, **109**, 55—67. Compare T., 1914, **105**, 2330; 1915, **107**, 233).—In order to test the assumption that homogeneous catalysis is due to infra-red radiation emitted in quanta by the catalyst and absorbed by the reacting substances, comparative measurements have been made of the wave-lengths of the bands in the infra-red absorption spectra of water and of aqueous solutions of hydrogen chloride, potassium chloride, and methyl acetate over the range $1\,\mu$—$2{\cdot}1\,\mu$.

The spectra of the solutions of these three substances are very similar, in that in all cases the bands occur at $1{\cdot}12\,\mu$, $1{\cdot}55\,\mu$, and $2{\cdot}1\,\mu$ (approximately), and thus correspond with the bands of the solvent ($1{\cdot}0\,\mu$, $1{\cdot}50\,\mu$, and $2{\cdot}0\,\mu$) with a slight displacement in every case in the direction of greater wave-length. The acid and salt solutions differ, however, in other respects, for the absorption of

hydrogen chloride solutions increases with the concentration, whereas solutions of potassium chloride show diminished absorption with increasing salt concentration.

It is suggested that the observed relations are to be attributed to the formation of additive compounds between the solute and the solvent. The greater absorption of hydrogen chloride as compared with potassium chloride solutions is said to be in agreement with the radiation theory of catalysis in that a positive catalyst is one which increases the radiation density at certain wave-lengths in the infra-red region, and it is known that an absorption band increases the radiation density below the band and diminishes it above the band. H. M. D.

Studies in Catalysis. IV. Stoicheiometric and Catalytic Effects due to the Progressive Displacement of One Reactant by Another in the "Acid" Hydrolysis of Methyl Acetate. ROBERT OWEN GRIFFITH and WILLIAM CUDMORE MCCULLAGH LEWIS (T., 1916, **109**, 67—83. Compare preceding abstract).—Earlier experiments on the rate of hydrolysis of methyl acetate in presence of an acid catalyst have shown that the velocity-coefficient k, calculated from the equation $k=1/t\,.\log a/(a-x)$, increases very appreciably with the concentration of the ester. New measurements have been made with varying concentrations of methyl acetate and with hydrochloric acid and trichloroacetic acid as catalysts which confirm this result. Since the reaction is really bimolecular and reversible, the velocity is represented by the equation

$$dx/dt=k_1(b-x)(w-x)-k_2x^2,$$

in which b is the initial concentration of the ester, w that of the water, and k_1 and k_2 are the coefficients of the opposed reactions. The data show that k_1 also increases with the concentration of the ester. The increase in k and k_1 cannot be accounted for by correcting the velocity-coefficients for the change which takes place in the degree of ionisation of the acid with increasing ester concentration.

On the assumption that the reactive substance is an additive compound of ester and water, the observed increase in the velocity-coefficients with increasing ester concentration can be explained in terms of the greater dissociating power of water in comparison with that of methyl acetate. In this sense the water exerts a negative catalytic effect, in that it tends to reduce the quantity of the reactive complex.

Incidentally, measurements were made of the equilibrium constant, $K=$[ester][water]/[methyl alcohol][acetic acid]. In hydrochloric acid solutions not exceeding $1N$, the mean value of K is 4·6. H. M. D.

History of Sympathetic Inks. L. VANINO (*Arch. Pharm.*, 1916, **253**, 505—511).—Instances are given of the use of sympathetic inks as far back as 230 B.C. C. S.

Inorganic Chemistry.

Preparation of Iodine Monochloride. JOSÉ J. CERDEIRAS (*Anal. Fis. Quim.*, 1915, **13**, 460—462).—Iodine monochloride is best prepared by passing dry chlorine over excess of iodine. It forms a red liquid, b. p. 102°. A. J. W.

Oxidation of Hydrogen Sulphide by Means of Ozone in Steam at 120°. U. BRESCIANI (*Ann. Chim. Applicata*, 1915, **4**, 343—346).—Under these conditions the oxidation of hydrogen sulphide to sulphuric acid is not complete, even when the ozonised air is in very large excess. T. H. P.

Sulphites, Thiosulphates, and Polythionates. III. Action of Mercuric Chloride on Sulphurous Acid, Sulphites, Thiosulphates, and Polythionates. A. SANDER (*Zeitsch. angew. Chem.*, 1916, **29**, 11—12, 16).—In previous work on this subject (A., 1915, ii, 161, 629) the author has assumed that the statement of Feld (A., 1911, ii, 289, 769) is correct, namely, that the action of mercuric chloride on thiosulphates and polythionates is an oxidising one, as expressed, for example, by the equation: $Na_2S_3O_6 + 2HgCl_2 + 2H_2O = Na_2SO_4 + Hg_2Cl_2 + 2HCl + H_2SO_4 + S$. This is apparently supported by the fact that the precipitate obtained is white. Further investigation, however, supports the older statements of Herschel, Rose, and Kessler (1819–1849) that the white precipitate obtained is the compound $Hg_3S_2Cl_2$, formed by the interaction of mercuric sulphide and the excess of mercuric chloride, the reactions taking place according to the equations: $2Na_2S_2O_3 + 3HgCl_2 + 2H_2O = Hg_3S_2Cl_2 + 4NaCl + 2H_2SO_4$; $2K_2S_3O_6 + 3HgCl_2 + 4H_2O = Hg_3S_2Cl_2 + 4KCl + 4H_2SO_4$; $2K_2S_4O_6 + 3HgCl_2 + 4H_2O = Hg_3S_2Cl_2 + 4KCl + 4H_2SO_4 + 2S$. The same amount of acid is liberated as according to Feld's equations, so that previous estimations depending on acidimetry are correct.

The validity of the last equations was proved by weighing the quantity of precipitate obtained in various experiments, the precipitate consisting of the compound $Hg_3S_2Cl_2$, mixed, in the case of the tetrathionate, with sulphur.

The estimation of a mixture of trithionate and tetrathionate can be best carried out as follows: The solution is oxidised with hydrogen peroxide in the presence of a known excess of sodium hydroxide, the reactions being: $Na_2S_3O_6 + 4H_2O_2 + 4NaOH = 3Na_2SO_4 + 6H_2O$; $Na_2S_4O_6 + 7H_2O_2 + 6NaOH = 4Na_2SO_4 + 10H_2O$. The unused alkali is then titrated. Another sample of the solution is heated with mercuric chloride (*loc. cit.*) and the acid liberated is estimated. From these two results it is easy to calculate the amounts of tri- and tetra-thionate present. T. S. P.

Constitution of Thio-salts. G. CESÀRO (*Chem. Zentr.*, 1915, ii, 874; from *Bull. Soc. franc. Minéral.*, 1915, **38**, 38—74).—The

author discusses the structural formulæ of thio-salts, $R_2^{III}S_3,mR^{II}S$, where R^{III} represents As, Sb, Bi, Fe, etc., and R^{II}, Cu_2, Pb, Hg, etc.; m is termed the basicity of the thio-salt and varies from $\frac{1}{3}$ to 12. The various types of thio-salts are considered in relation to natural minerals, especially argentiferous pyrites, pyrrhotite, and berthierite. The natural thio-salts are divided into the following types: poly-salts, in which m is less than 1; meta-salts, with $m=1$; salts intermediate to meta- and pyro-salts, m lying between 1 and 2; pyro-salts, with $m=2$; salts intermediate to pyro- and ortho-salts, m being between 2 and 3; ortho-salts, with $m=3$; argentiferous pyrites, which represent molecular mixtures of a poly-salt, having $m=\frac{1}{3}$, with an ortho-salt; basic thio-salts, with m between 3 and 4; and perbasic thio-salts, with m between 5 and 12. T. H. P.

Baeyer's Tension Theory and the Structure of the Diamond ERNST MOHR (*Chem. Zentr.*, 1915, ii, 1065; from *Sitzungsber. d. Heidelberger Akad. Wiss. Mathem. naturwiss. Kl.* [Abt. A], 1915, **7**, 18 pp.).—The author's considerations are based on Sachse's theory, according to which two different tension-free forms of *cyclo*-hexane are conceivable, with the atoms of the ring not in one plane. Sachse's models are not at variance with observation if it is assumed that impacts with other molecules are sufficient to give to the *cyclo*hexane ring all the possible forms in turn; the number of isomerides with *cyclo*hexane and its substitution products are, then, with tension-free arrangement of the carbon atoms, the same as if the atoms of the ring were situated permanently in one and the same plane. The case of tension-free ring-combinations, in which several carbon atoms of one *cyclo*hexane ring belong also to another ring, is explained. Superposition of a number of such combinations leads to large carbon atom systems of simple, regular structure, all the carbon valencies in the interior being satisfied without tension; only at the surface of the system do valencies protrude unsatisfied into space. In one form of this model the six atoms of each *cyclo*hexane ring stand exactly above the six ring-atoms of the next lower layer ("gerader Bau"); in a second possible form the rings are so arranged that the centre of each lies immediately above a ring carbon atom of the adjacent layer ("schiefer Bau"). The latter carbon atom system is identical with the space-lattice of the diamond derived by Bragg from the reflection of X-rays by crystals (*Proc. Roy. Soc.*, 1913, [*A*], **89**, 277). The constitution of graphite may be regarded as corresponding either with the direct superposition of the *cyclo*hexane rings or with a space-lattice in which the structure is alternately direct and oblique. T. H. P.

The Electrolysis of an Aqueous Solution of Potassium Orthosulphoantimonite [Potassium Thioantimonite], and the Constitution of this Compound. J. A. MULLER (*Bull. Soc. chim.*, 1916, [iv], **19**, 3—8).—In the experiments the cathode was of antimony and the anode of platinum. In the first series both electrodes were in the solution of the thioantimonite, whilst in the

second series only the cathode was in this solution, the anode being in a 17% solution of sodium hydroxide, the two solutions being separated by a porous diaphragm, which was impregnated with the solution of the thioantimonite. In the first series of experiments a precipitate of antimony was obtained at the cathode together with a feeble evolution of gas, whilst at the anode a precipitate of antimony sulphide containing a little free sulphur and some potassium sulphide was obtained. The results of the second series of experiments show that, during the electrolysis, there do not pass from the cathode cell to the anode cell any negative ions containing potassium, but there does pass in this direction a certain weight of a grouping corresponding with the formula SbS_3. The author considers that these results indicate that the original compound is really the combination of the radical SbS_3 with three atoms of potassium, and not the combination of three negative groups KS with an atom of antimony. W. G.

Approximate Determinations of the Boiling Points of some Alkali Haloids. L. H. BORGSTRÖM (*Jahrb. Min.*, 1915, ii, Ref. 298; from *Tidskriften Teknikern*, 1915, **24**).—The following values are the means of several determinations, which varied 10—20°:

LiCl ...... 1360°	NaCl ...... 1490°	KCl ...... 1500°
	NaBr 1455	KBr 1435
	NaI 1350	KI......... 1420

L. J. S.

The Constitution of Brasses Containing Small Percentages of Tin. O. F. HUDSON and R. M. JONES (*J. Inst. Metals*, 1915, **14**, 98—115).—That portion of the ternary system copper–zinc–tin has been examined, which includes alloys containing from 50% to 70% of copper and from 0% to 5% of tin. An equilibrium diagram for this region has been determined. There are no distinct differences between the γ constituent of the brasses and the δ constituent of the bronzes, and the two substances appear to pass continuously into one another. The constituent which appears light blue under the microscope may thus be termed γ when in contact with β', or δ when in contact with α. C. H. D.

The Copper-Rich Kalchoids. SAMUEL L. HOYT and PAUL H. M. P. BRINTON (*J. Inst. Metals*, 1915, **14**, 178—188. Compare A., 1914, ii, 366; Hudson and Jones, preceding abstract).—The position of the eutectoid line in the copper–zinc–tin alloys has been further determined, and the system is shown to be truly ternary. Both thermal curves and microscopical examination are employed. C. H. D.

The Micro-chemistry of Corrosion. IV. Gun Metal. CECIL H. DESCH and HENRY HYMAN (*J. Inst. Metals*, 1915, **14**, 189—198. Compare A., 1914, ii, 367, 655; 1915, ii, 689).—The corrosion of

copper–tin alloys containing zinc has been examined by the method previously described. The total corrosion is much less than that of the brasses under similar conditions, and the course varies in a marked degree with the applied *E.M.F.* When the current is small, only the α-phase is attacked, but with larger currents the eutectoid is also corroded. The protective action of the layer of basic tin salts is strongly marked. The α-constituent develops a distinct crystalline structure during corrosion. In quenched alloys containing α and β there is very little difference between the two constituents in their rate of corrosion. C. H. D.

Polyiodides. III. The System $CuI—I_2$. R. KREMANN and V. BORJANOVICS (*Monatsh.*, 1915, **36**, 923—927. Compare A., 1913, ii, 15).—Cooling curves for mixtures of cuprous iodide and iodine, previously heated for several hours at temperatures varying from 180° to 240°, have shown no evidence of the formation of any compound. The only change indicated by these curves corresponds with the freezing point of iodine at 114°. This result has been confirmed by measurements of the vapour pressure of the iodine in equilibrium with the above mixtures at 26°. The values obtained were identical with the vapour pressure of pure iodine.
H. M. D.

Aluminium.—Aluminates. ERNST MARTIN (*Mon. Sci.*, 1915, [v], **5**, 225—232).—Aluminium hydroxide produced by the hydrolysis of aluminates is quite different in properties from that produced by the precipitation of solutions of aluminium salts with ammonium hydroxide. It is of a sandy nature, non-hygroscopic, and when dry has a composition corresponding with the formula $Al_2O_3,3H_2O$. On heating, it commences to lose water at about 160°; at 225° it contains $2H_2O$, and at 235° $1H_2O$, but it is only completely dehydrated in the neighbourhood of 1000°; the loss of water during heating does not take place at a uniform rate. The partly dehydrated hydroxide takes up water again on exposure to the air to the extent of half that which has been lost, but this water is readily removed in a desiccator or on heating at 100°. The author endeavours to explain these results by means of constitutional formulæ.

The hydroxide obtained by precipitation with ammonium hydroxide, when dried at 80°, has a composition approaching that of $Al_2O_3,2H_2O$. The loss of water on heating takes place fairly uniformly, and it is impossible to say that at any particular temperature a definite hydrated oxide exists.

When mixtures of alumina and barium carbonate, no matter in what proportions, are heated at temperatures not exceeding 1500°, the aluminate Al_2O_3,BaO is always formed. At the temperature of the electric arc, *tribarium aluminate*, $Al_2O_3,3BaO$, is obtained from a mixture of alumina and barium carbonate in the molecular proportions of 1 : 3. It is soluble in water, and the solution gives with calcium chloride a precipitate of the formula $(Al_2O_3,3CaO)_5,3CaCl_2$. Solutions in water of the product obtained by heating mixtures of

alumina and barium carbonate at temperatures up to 1500° are not stable, and slowly deposit aluminates which are less and less rich in barium. From a solution made from alumina and barium carbonate in the molecular proportions of 1 : 1, on concentration, a *barium aluminate*, $10Al_2O_3,11BaO,55H_2O$, can be obtained as needles; by precipitation with alcohol an *aluminate* (doubtful whether pure), $5Al_2O_3,4BaO,4H_2O$, is obtained.

Dicalcium aluminate, $Al_2O_3,2CaO$, is obtained by heating a mixture of alumina and calcium carbonate in the molecular proportion of 1 : 2 at 1500°. By appropriate variation of the composition of the mixture used, the aluminates Al_2O_3,CaO, $Al_2O_3,3CaO$, $2Al_2O_3,3CaO$, $5Al_2O_3,6CaO$, and $10Al_2O_3,11CaO$, have been obtained, but not properly investigated. Their solubility in water is very small.

Double aluminates of the alkali metals and alkaline earth metals can be obtained by heating mixtures of alumina, alkaline earth carbonates, and sulphates or chlorides of the alkali metals. From mixtures of alumina, barium sulphate or calcium sulphate, and carbon, *sulphido-aluminates* are obtained, of which the following have been isolated: $Al_2O_3,2BaS$; $2Al_2O_3,3BaS$.

A mixture of silica, alumina, and calcium carbonate in the molecular proportion of 2 : 1 : 2 when heated to 1400° gives the *silico-aluminate*, $2SiO_2,Al_2O_3,2CaO$, which is insoluble in water. Under similar conditions, using the molecular proportion 2 : 1 : 1, the *silico-aluminate*, $2SiO_2,Al_2O_3,CaO$, is obtained. T. S. P.

The Conservation in the Cold of Solutions of Sodium Aluminate. G. A. Le Roy (*Compt. rend.*, 1916, **162**, 74—75).—Concentrated solutions of sodium aluminate, which slowly decompose when allowed to remain at the ordinary temperature, can be kept unaltered for an indefinite time at $-1°$ to $-2°$ in an ice-chest. W. G.

Constitution of Ultramarine. Heinrich Puchner (*Kolloid Zeitsch.*, 1915, **17**, 119—123).—In the course of experiments on the effect of sodium chloride solutions on various types of soil it has been found that, when calcareous sand containing humus and gypsum, obtained from the neighbourhood of Münich, is subjected to the action of sodium chloride solution in such a way that the solution is drawn up through the soil by capillary action, the aqueous extracts from the middle portion of the soil yield a residue which on ignition exhibits the dark blue colour characteristic of ultramarine. Analyses of such residues show that the development of the blue colour is connected with the proportion of sulphate in the residue. The general behaviour of the residues seems to show conclusively that the blue colour is really due to the formation of ultramarine. If the sodium chloride is replaced by potassium chloride the effect is not obtained.

The observations are discussed in reference to whether ultramarine is a definite chemical compound or whether the blue colour is connected with adsorption phenomena, but no definite conclusion is drawn. H. M. D.

Anhydrous Sulphates. VIII. Manganous Sulphate with Lithium, Sodium, and Potassium Sulphates. G. CALCAGNI and D. MAROTTA (*Gazzetta*, 1915, **45**, ii, 368—376. Compare A., 1914, ii, 52, 205).—The fusion diagrams of the systems $MnSO_4$–Li_2SO_4, $MnSO_4$–Na_2SO_4, and $MnSO_4$–K_2SO_4 have been investigated. The first yields no compound between its constituents, but the others give: $3MnSO_4,Na_2SO_4$, $MnSO_4,3Na_2SO_4$, and $2MnSO_4,K_2SO_4$.

T. H. P.

The Influence of Oxygen on Some Properties of Pure Iron. WESLEY AUSTIN (*J. Iron Steel Inst.*, 1915, **92**, 157—163).—Alloys of iron and oxygen are prepared by melting together iron and ferric oxide in a small arc furnace lined with magnesia. The product does not in any case contain more than 0·288% of oxygen. The A3 point is lowered by oxygen, but the A2 point is unchanged. Pearlite is absent. Microscopical examination shows that the oxide is mechanically mixed, appearing in globules. The alloys may be worked above 900° or between 750° and 850°, but are brittle between those temperatures.

'Blue-brittleness' occurs as high as 700° The alloys are very resistant to atmospheric corrosion, but are more readily attacked by acids than mild steel.

C. H. D.

Sulphur in Malleable Cast Iron. R. H. SMITH (*J. Iron Steel Inst.*, 1915, **92**, 141—156).—Sulphur is not removed from white iron in the ordinary annealing process, whether the surrounding mixture be reducing, oxidising, or neutral. When oxidation takes place, the sulphur tends to diffuse into the unoxidised portions of the iron. Sulphur does not produce an injurious effect until its quantity exceeds 0·15%.

C. H. D.

The Occurrence and Influence of Nitrogen in Iron and Steel. N. TSCHISCHEVSKI (*J. Iron Steel Inst.*, 1915, **92**, 47—105).—For the estimation of nitrogen in iron or steel the metal is dissolved in hydrochloric acid, the solution made alkaline with lime, and the ammonia in the distillate estimated by means of Nessler's reagent, or by titration with *N*/100-sulphuric acid. The addition of zinc, which is sometimes recommended, is to be avoided. None of the nitrogen of the metal passes off as nitrogen oxides. A tin tube should be used for the distillation, on account of the alkalinity of glass.

Iron in powder or filings reacts with dry ammonia at 200°, the maximum rate of absorption being at 450°, the compound formed being Fe_2N. Carbon is practically without influence on the absorption of nitrogen. Manganese reacts with ammonia at 600—700° with considerable development of heat, forming the compound Mn_3N_2, and finally MnN. Manganese also reacts with dry nitrogen, but more slowly. Manganese nitride is soluble in molten iron. Silicon nitride also dissolves in iron, and as this compound is very stable, it remains in the residue when the steel is dissolved in acid for the purpose of analysis, and so introduces an error into the

estimation of nitrogen. Aluminium nitride passes into solid solution in iron.

The cementation of iron by ammonia leads to the formation of a brittle layer of nitride, whilst the interior of the metal contains crystals of the same substance. Nitrogen hardens steel, and decreases its ductility. C. H. D.

Phosphorus in Iron and Steel. W. H. HATFIELD (*J. Iron Steel Inst.*, 1915, **92**, 122—140. Compare Stead, A., 1915, ii, 778).—White irons containing about 2·9% of carbon are little changed in properties by the presence of phosphorus in quantities up to 0·20%. Above 0·25% free phosphide makes its appearance. When such iron is etched by means of Stead's copper reagent, the variations of deposition which are obtained may be due to the irregular distribution of other elements besides phosphorus. C. H. D.

The Carburisation of Iron at Low Temperatures. T. H. BYROM (*J. Iron Steel Inst.*, 1915, **92**, 106—121).—Mild steel, exposed for several years to the action of blast-furnace gases at about 500°, becomes converted almost completely into carbides, analysis indicating a mixture of Fe_3C and Fe_2C. Electrolytic iron strips are readily carburised by carbon monoxide at 550—600°. A layer of iron sulphide is also formed on the specimens exposed to blast-furnace gas. In the interior of the metal, the carbide is formed at the boundaries of the crystal grains. C. H. D.

The Influence of Heat Treatment on the Specific Resistance and Chemical Constitution of Carbon Steels. EDWARD D. CAMPBELL (*J. Iron Steel Inst.*, 1915, **92**, 164—180).—The specific resistance of carbon steels increases with the temperature from which they are quenched. This is in accordance with the view that the dissolved carbides dissociate with rising temperature (*J. Iron Steel Inst.*, 1899, ii, 223). A steel containing 0·35% of carbon, quenched from different temperatures, shows a close parallelism between the specific resistance and the colour produced by the solution of the same specimens in cold nitric acid. When steels are regarded as solid solutions, sufficient attention is not usually given to the solute. The study of aqueous solutions is not regarded as that of the influences of various solutes on the properties of water, but the properties of steel are commonly treated as modifications of those of iron by the presence of dissolved molecules. The term "ionoids" is used to denote the products of dissociation of the solutes in metallic solid solutions. The effect of the ionoids is to increase the specific resistance of the solvent metal. C. H. D.

Mixed Crystals of Iron Ammonium Chloride. O. LEHMANN (*Jahrb. Min.*, 1915, ii, 109—132).—A detailed summary of the literature and of the views previously expressed by the author. L. J. S.

Synthesis of Smaltite and Löllingite. A. BEUTELL and FR. LORENZ (*Centr. Min.*, 1916, 10—22).—Smaltite and löllingite (A.,

1915, ii, 639) after being heated in a vacuum until no further loss of arsenic occurred, were the materials experimented on, the ratio of (Co, Ni, Fe) : As and of Fe : As being thereby reduced to 1 : 0·95 and 1 : 0·88 respectively. These, and also pure cobalt, were heated in an atmosphere of arsenic at various temperatures for prolonged periods until equilibrium was attained. Using pure cobalt, the following arsenides were obtained, the range of temperature through which they are stable in arsenic vapour being indicated in brackets: $CoAs$ (275—335°), Co_2As_3 (345—365°), $CoAs_2$ (385—405°), Co_2As_5 (415—430°), and $CoAs_3$ (450—618°). The iron arsenides obtained under these conditions were: $FeAs$ (335—385°), Fe_2As_3 (395—415°), and $FeAs_2$ (430—618°). The varying compositions of the minerals smaltite, chloanthite, skutterudite, and löllingite are explained by the mixture of these various arsenides. L. J. S.

The Explosive Property of Uranyl Nitrate. ARNO MÜLLER (*Chem. Zeit.*, 1916, **40**, 38—39).—The author was unable to confirm the detonation or decrepitation of preparations of uranyl nitrate crystallised from ether as specific properties of that substance. In only three out of twenty experiments was any detonation observed on mechanical handling of the preparations after moistening with water, and in no case with the violence described by Ivanov (A., 1912, ii, 455) or Andrews (A., 1913, ii, 60). The phenomenon was never observed in the case of preparations recrystallised from water, or prepared in the absence of free nitric acid, and the opinion is advanced that it may be due to the decomposition of an unstable compound of a lower oxide of nitrogen with a uranium–ether additive compound. G. F. M.

Densities of Solutions of Uranium Nitrate in Water, in Alcohol, and in Some Acids. W. ŒCHSNER DE CONINCK (*Bull. Soc. chim.*, 1915, [iv], **17**, 422—424).—The author has determined the densities of solutions of uranium nitrate in water, alcohol (85%), commercial methyl alcohol, acetic acid (D 1·055), nitric acid (D 1·153), sulphuric acid (D 1·138), and hydrobromic acid (D 1·21), containing varying percentages of the salt. The results are tabulated in detail in the original. W. G.

The Preparation of Metallic Vanadium. R. EDSON and D. MCINTOSH (*Trans. Roy. Soc. Canada*, 1915, [iii], **9**, 81—83).—The method described, whilst inapplicable for the preparation of vanadium on a large scale, may be used with advantage in the laboratory, or for demonstration in the lecture-room.

A flask, containing some vanadyl chloride, is fitted with a platinum wire filament, attached to two heavy copper leads, and also with inlet and exit tubes for the passage of a current of dry hydrogen. The filament is made to glow by passing a current through it, and the vanadium is deposited smoothly on the platinum as a silvery-grey coating.

The experiment may be carried out either in a vacuum or in an atmosphere of hydrogen at low pressure. As soon as the filament

reaches a white heat the deposition begins, and can be continued until the wire burns out.

The vanadyl chloride is made by heating a mixture of the pentoxide and charcoal in a stream of chlorine, and need not be purified from any vanadium tetrachloride it contains. T. S. P.

Antimony Pentachloride and Iodine. OTTO RUFF [with J. ZEDNER and LEOPOLD HECHT] (*Ber.*, 1915, **48**, 2068—2076).—In an earlier paper (A., 1909, ii, 1023) it was mentioned that antimony pentachloride reacts with iodine, but not with bromine. The author hoped to make a complete study of this reaction, but has had to desist because of the effect of the vapours on the respiratory organs. Recently, however, Moles (A., 1914, ii, 812) has studied the depression of the freezing point of antimony pentachloride when iodine, iodine monochloride, or iodine trichloride are dissolved in it, and his results help to elucidate the above reaction.

Three main reactions proceed, as indicated by the equations: (I) $SbCl_5 + 2I = SbCl_3 + 2ICl$; (II) $2SbCl_5 + 2I = SbCl_5,2ICl + SbCl_3$; (III) $3SbCl_5 + 4I = SbCl_5,3ICl + 2SbCl_3 + ICl$. Equation I represents the reaction which takes place when less than 1·5% of iodine is dissolved in the antimony pentachloride. Some iodine trichloride, antimony tri-iodide, and possibly a chloro-iodide of quinquevalent antimony are formed in addition, but no evidence can be adduced of the formation of a compound, $SbCl_5I$, analogous to SbF_5I.

The *compounds* $SbCl_5,2ICl$ and $SbCl_5,3ICl$ may be isolated by sublimation from a mixture of antimony pentachloride (10 grams) and iodine (4·3 or 8·6 grams) under 15 mm. pressure, from a bath at 30—35°. They form bluish-black crystals, stout prisms or needles, m. p. 62—63°, which fume in the air, and dissolve readily in carbon tetrachloride or chloroform, but sparingly in antimony pentachloride. In the solutions they are strongly dissociated.

Temperature-concentration diagrams of mixtures of antimony pentachloride and iodine monochloride were also made, in order to confirm the existence of the above double compounds. J. C. W.

Presence of Platinum in Spain. DOMINGO DE ORUETA and S. PIÑA DE RUBIES (*Compt. rend.*, 1916, **162**, 45—46. Compare this vol., ii, 106).—The Ronda chain, occurring in Andalusia between Malaga and Gibraltar, is constituted by a series of rocks very similar in constitution and distribution to those forming the Ural platiniferous beds. The central zone of peridotites is 72 kilometres long by 20 kilometres broad, and is surrounded by other smaller ones. Microscopic examination further confirms the analogy between these rocks and those of the Urals, particularly in the case of the dunite. The mean of fifty analyses gives the platinum content as 3 grams per cub. metre of platiniferous sand, the variation being from traces up to 28 grams. W. G.

Silver–Platinum Alloys and their Analysis. IDE KOIFMANN. (*Arch. Sci. phys. nat.*, 1915, [iv], **40**, 509—513).—The action of nitric acid on silver–platinum alloys was investigated; the alloys

used contained from 0·219 to 5·162% of platinum, and were prepared by heating together mixtures of silver and platinum for twenty minutes at a temperature above the fusing point of silver, the mixtures being covered with a layer of pure sodium chloride. The preparation of the alloys confirmed the slight solubility of platinum in silver, and it was impossible to make an alloy containing much more than 5% of platinum. When these alloys were boiled with nitric acid of varying concentrations, a brown-coloured solution was obtained, together with a more or less voluminous, black sediment, and the latter always yielded a brown-coloured solution when treated with water. The author considers that silver and platinum in an alloy cannot be separated by means of nitric acid; part of the platinum forms a colloidal solution in the nitric acid, and the remainder also passes into solution when treated with a sufficient quantity of water. W. P. S.

Mineralogical Chemistry.

Errors in Silicate Analyses: Composition of Alkali-free Aluminous Augites. G. TSCHERMAK (*Centr. Min.*, 1916, 1—9).—General remarks on the errors in the methods used in analysis, personal errors, and errors due to impurities of the material. Analyses made by different authors on the same sample of material or of a mineral from the same occurrence are compared and criticised. A further reply to Boeke (A., 1911, ii, 283) regarding the components assumed to enter into the composition of the alkali-free aluminous augites, and a criticism of the analyses plotted in his diagrams, many of which are rejected as untrustworthy. The author still maintains that the condition $p=q+r$ holds in the formula $p SiO_2,q MgO,r CaO,s Al_2O_3$. L. J. S.

Identity of Kalk-Cancrinite and Meionite. L. H. BORGSTRÖM (*Jahrb. Min.*, 1915, ii, Ref. 310; from *Öfvers. Finska Vet. Soc. Förh.*, 1915, **57**, Afd. A, No. 6, 1—3).—Lemberg's (1876) analysis of kalk-cancrinite from Vesuvius agrees very closely with Borgström's carbonate-meionite, $CaCO_3,3CaAl_2Si_2O_8$ (A., 1915, ii, 836). The physical characters and paragenesis are also in agreement. L. J. S.

Manganese in Some Springs in the Alps. F. JADIN and A. ASTRUC (*Compt. rend.*, 1916, **162**, 196—197).—The authors have examined the waters from fifteen springs in the Alps for manganese, and find that they are, on the whole, poorer in manganese than the natural waters of the Central Plateau, but richer than those of the Vosges mountains (compare A., 1914, ii, 378, 739). The presence of iron exerts a marked influence on the manganese content, increasing it considerably. W. G.

Analytical Chemistry.

Use of Centrifugal Apparatus in Chemical Analysis. OTTO NOLTE (*Landw. Versuchs-Stat.*, 1915, **87**, 449—457).—The author gives many instances in which the centrifugal apparatus possesses advantages over the filter for the separation of precipitates from liquids; in many cases precipitates can be much more rapidly and accurately separated by centrifugal action than by filtration. A centrifugal apparatus is described in which the separations are effected in small silica beakers or other vessels, suitable mountings being provided for these in the centrifugal drum. W. P. S.

New Form of Gas Burette. HAMMERMANN (*Chem. Zeit.*, 1916, **40**, 84).—A gas-measuring burette and a levelling tube are connected at their lower ends with a **Y**-tube, the stem of which is fitted into one neck of a three-necked Woulfe's bottle; the centre opening of the latter carries a three-way tap connected with a caoutchouc pressure bulb, and a thermometer is fitted into the other neck. The Woulfe's bottle is filled with the absorption solution; this is forced up into the burette and levelling tube by means of the pressure bulb; the tap at the top of the burette is then closed, and the level of the solution is adjusted by means of the tap on the centre neck of the bottle, this also serving for the escape of air from the bottle when the gas under examination is admitted to the burette. A tubulure is provided at the bottom of the bottle.
W. P. S.

Potassium Hydrogen Carbonate as a Standard in Acidimetry and Alkalimetry. G. INCZE (*Zeit. anal. Chem.*, 1915, **54**, 585—602).—Potassium hydrogen carbonate is most readily prepared by passing a current of carbon dioxide into an alcoholic solution of potassium hydroxide; the salt is then recrystallised by treating its aqueous solution with alcohol. It should be stored in well-closed, perfectly dry bottles, and under these conditions does not undergo any change; in the presence of moisture, however, it loses carbon dioxide. On account of its high molecular weight and the readiness with which it may be obtained in a pure condition, the salt forms a suitable basis for standardising acid solutions. W. P. S.

Estimation of Oxygen (in Water) by Winkler's Method. II. G. BRUHNS (*Chem. Zeit.*, 1916, **40**, 45—46, 71—73. Compare this vol., ii, 47).—The following modifications of this method are recommended: Manganous sulphate solution (1 : 1) is used in place of manganous chloride solution, and potassium hydroxide–sodium hydroxide solution (1 : 1 : 2) in place of sodium hydroxide–potassium iodide solution. After the water has been treated with 10 drops of each of these solutions and the precipitate has settled, potassium iodide is added either in the form of crystals or as a concentrated

solution. The mixture is then acidified with dilute hydrochloric acid (1 : 1) or sulphuric acid (1 : 3), a definite volume of the water is withdrawn from the flask by means of a pipette, and the remainder is titrated with thiosulphate solution in the usual way. The influence of nitrites, etc., may be eliminated by adding solid potassium hydrogen carbonate after the manganese oxide precipitate has settled, collecting the precipitate on a filter, and then treating it with potassium iodide and acid. If the water contains ferric salts, phosphoric acid should be used instead of hydrochloric acid for acidifying the mixture; the water should be treated previously with permanganate if it contains ferrous salts. W. P. S.

Estimation of Sulphuric Acid in the Presence of Phosphoric Acid. TH. VON FELLENBERG (*Chem. Zentr.*, 1915, ii, 1262; from *Mitt. Lebensmittelunters. Hyg.*, 1915, **6**, 191—195).—The author confirms a statement by Baragiola and Godet that the results obtained in the estimation of sulphuric acid are too high if phosphoric acid is also present. The error may be reduced to a minimum if the barium chloride solution is added drop by drop, in not too great excess, to the boiling sulphuric acid or sulphate solution, which should contain about 0·13 c.c. of concentrated hydrochloric acid per 100 c.c. W. P. S.

The Volumetric Estimation of Total Sulphur and Sulphates in Small Quantities of Urine. JACK CECIL DRUMMOND (*Biochem. J.*, 1915, **9**, 492—507).—The benzidine method of Rosenheim and Drummond (A., 1914, ii, 485) for the estimation of urinary sulphates can be carried out with as little as 2 c.c. of urine by titrating the precipitated benzidine sulphate with 0·02*N*-alkali, provided certain details of technique, especially in the matter of filtration, are followed. The method is also applicable to the estimation of total sulphur in small quantities of biological material by applying the precipitation of the benzidine sulphate to the solution of salts obtained after oxidation of the material by Benedict's method.
W. D. H.

The Analysis of a Mixture of Alkali Sulphides, Thiosulphates and Dithionates. J. A. MULLER (*Bull. Soc. chim.*, 1916, [iv], **19**, 8—9).—Any sulphate present is first estimated by precipitation with barium chloride in a very dilute solution slightly acidified with acetic acid. The sulphur present as sulphide and thiosulphate is estimated by titrating an aliquot portion, suitably diluted and feebly acidified with acetic acid, with a standard iodine solution. Another portion is acidified with acetic acid and the hydrogen sulphide removed by evacuating the flask for ten minutes by means of a water-pump, the residual liquid being titrated with the standard iodine solution. From a fourth portion of the liquid the sulphide is removed as described and the liquid then made alkaline with potassium hydroxide, transferred to a silver capsule, and evaporated to dryness with a little potassium nitrate, the residue being gradually raised to a dull red heat. In this residue

the sulphate is estimated in the usual way. Owing to the presence of an excess of alkali sulphides, the only thionates likely to be present are the dithionates, and thus from the above data the necessary percentages can be calculated. W. G.

Simple Method for the Estimation of Nitrogen in Urine. VICTOR C. MYERS (*Chem. Zentr.*, 1915, ii, 858; from *Münch. med. Woch.*, 1915, **62**, 1076—1077).—A modification of Folin and Farmer's method (A., 1912, ii, 702) is described. The colorations are compared in an Autenrieth-Konigsberger colorimeter (A., 1910, ii, 910). W. P. S.

A Modification of the Lunge Nitrometer. W. SENFTEN (*Chem. Zeit.*, 1916, **40**, 39—40).—In order to obviate the necessity of dissolving the substance in the cup of the nitrometer in its usual form, the apparatus is modified by connecting the upper stop-cock with the decomposition tube with a ground glass joint. The stop-cock itself is triple bored, and the nitric oxide is measured externally by transference to a gas burette. The substance is dissolved in sulphuric acid in the decomposition tube, in a vacuum if necessary, after adjusting the mercury level to the stop-cock at the base of the tube, which is then turned off. When solution is complete the mercury is slowly admitted into the tube, thus expelling the air through the upper stop-cock, and the decomposition is then conducted in the usual way. A special reversible gas-measuring burette is also described, having a tap at each end, an enlargement at one end, and graduated through its entire length. If after absorption of one constituent of a gas mixture the remaining volume is so small that it is contained entirely within the enlarged bulb, the burette is simply reversed and the volume can then be read off on the second reversed scale. G. F. M.

Detection of Arsenic in Beverages. L. VUAFLART (*Ann. Falsif.*, 1915, **8**, 414—415).—The author states that 1 mg. of arsenic per litre of liquid can be detected by means of Bougault's reagent. To detect arsenic in beer, 250 c.c. of the sample are treated with a few drops of bromine, filtered after twenty-four hours, and the filtrate then mixed with 1 c.c. of saturated sodium phosphate solution, 5 c.c. of magnesia mixture, and 80 c.c. of ammonia. After twenty-four hours, the precipitate is collected, dissolved in 20 c.c. of nitric acid (1:4), the solution treated with 2 c.c. of 20% magnesium nitrate solution, and evaporated to dryness. The residue is then ignited, and heated with 10 c.c. of the reagent. A similar process is used for the detection of arsenic in wines. W. P. S.

Estimation of Arsenic in Urine, Blood, and Animal Organs. WILHELM KOSIAN (*Chem. Zentr.*, 1915, ii, 1311; from *Pharm. Post*, 1915, **48**, 321).—One hundred and fifty grams of urine, blood, or serum are evaporated to a syrup, and 50 grams of this, or the same quantity of finely divided animal substance, etc., are warmed with

20 c.c. of hydrochloric acid and a quantity of potassium chlorate; the excess of chlorine is then expelled, 10 grams of ferrous sulphate are added, the mixture is transferred to a distillation flask, and diluted to 200 c.c. with hydrochloric acid. The cold mixture is saturated with hydrogen chloride and then distilled in a current of the same gas until 80 c.c. of distillate have been collected in a receiver containing 50 c.c. of water. The distillate is now diluted to 200 c.c., and 10 c.c. of it are treated with 3 c.c. of concentrated hydrochloric acid, methyl-orange is added, and the mixture is titrated with $N/10$- or $N/100$-potassium bromate solution until it is colourless (compare Győry, A., 1893, ii, 554). W. P. S.

Formulæ for Use in the Indirect Analysis of Generator Gas. FRITZ HOFFMANN (*Chem. Zeit.*, 1916, **40**, 81—82).—The following formulæ are given for calculating the proportions of carbon monoxide, hydrogen, and methane in generator gas after the carbon dioxide and oxygen have been removed. Let V be the total volume of the three gases, K the volume of the carbon dioxide formed when they are burnt together, C the contraction in volume, S the volume of oxygen required for the combustion, then:

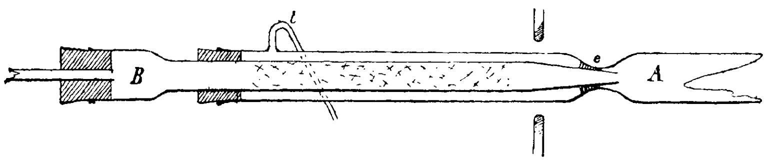
	A.	B.	C.	D.
Being given;	$V, K, C.$	$K, C, S.$	$C, S, V.$	$S, V, K.$
$CO =$	$2K/3+V-2C/3$	$4K/3+C/3-S$	$4V/3+S/3-C$	$K-2S/3-V/3$
$H_2 =$	$V-K$	$C-S$	$C-S$	$V-K$
$CH_4 =$	$2K/3+2C/3-V$	$S-K/3-C/3$	$2S/3-V/3$	$2S/3-V/3$

The formulæ A and B are principally used, since the values C and K are determined directly in the course of the analysis. W. P. S.

Fractional Combustion of Gases over Copper Oxide. E. TERRES and E. MAUGUIN (*Chem. Zentr.*, 1915, ii, 1309; from *J. Gasbeleucht.*, 1915, **58**, 8—11).—Hydrogen is oxidised completely when passed over copper oxide at 250—300°, but carbon monoxide is oxidised at 305° only to the extent of 90—94%. A mixture of equal volumes of hydrogen and carbon monoxide is burnt completely at 300°. Acetylene and ethylene, even when mixed with hydrogen, do not burn quantitatively at 300°; a quantity of carbon separates. Benzene behaves in a similar manner. Methane begins to burn at 310°, and the presence of hydrogen lowers this temperature by a few degrees. Pure methane is oxidised completely at a red-heat, and the presence of hydrogen is without influence. A mixture of carbon monoxide and methane cannot be separated by fractional combustion, but this is possible in the case of a mixture consisting of equal volumes of carbon monoxide and hydrogen on the one hand and methane on the other. In using the Drehschmidt-Ubbelohde apparatus, notice should be taken of the fact that at high temperatures copper oxide loses oxygen, and that this may lead to error. W. P. S.

A New Method for the Simultaneous Estimation of Carbon, Hydrogen, and Mercury in Organo-mercuric Compounds. V. GRIGNARD and A. ABELMANN (*Bull. Soc. chim.*, 1916, [iv], **19**, 25—27).—The ordinary combustion tube A is modified, as shown

in the sketch, at the exit end. It is slightly constricted at *e* just before it leaves the furnace, and then is allowed to project 20 cm. beyond this. In this external portion is fitted the tube *B*, held in position at the open end by a rubber stopper and at the constriction by a cone of calcined asbestos. *B* contains a spiral of gold wire and is weighed before and after the experiment and during the combustion, and is kept slightly heated to prevent the condensation



of water. Round the tube *B*, by means of the narrow tube *t*, is kept passing a slow current of dry oxygen at a pressure slightly higher than that existing in the major part of *A* in order to prevent any leakage of water or mercury vapours through the asbestos stopper at *e*. The carbon dioxide and water vapour are collected and weighed as usual. W. G.

Can Carbon Dioxide in Sea Water be Directly Estimated by Titration? SERGIUS MORGULIS and EVERETT W. FULLER (*J. Biol. Chem.*, 1916, **24**, 31—35).—In recent investigations of the metabolism of marine organisms Moore and his collaborators have estimated the amount of carbon dioxide produced in the water by titration with a centinormal solution of an alkali. The authors believe that this method is so inaccurate as to invalidate the conclusions based on its results, and quote results of experiments which, in their opinion, show that only approximately one-third of the carbon dioxide can be determined under such conditions. They also suggest that an indirect method of estimation, based on precipitation of the carbon dioxide with *N*/5-barium hydroxide solution and the titration of the excess of this reagent with *N*/10- or *N*/50-acid, is susceptible of development to greater accuracy.

D. F. T.

A Copper Cathode and Iron Anode in the Electro-analysis of Brass. J. GUZMÁN and J. M. FERNÁNDEZ LADREDA (*Anal. Fis. Quim.*, 1915, **13**, 308—315).—An account of the results obtained in the electrolytic analysis of cartridge cases. A. J. W.

Analysis of Copper–Aluminium–Zinc Alloys. H. GRAEFE (*Chem. Zeit.*, 1916, **40**, 102).—The following method is suggested for the analysis of alloys consisting approximately of copper, 25—27%, aluminium, 14—18%, and zinc, 54—57%, together with traces of silicon, cadmium, tin, lead, and iron. A quantity of 0·5 gram of the turnings is dissolved in 15 c.c. of nitric acid (D 1·4), the solution is diluted, and metastannic acid is separated by filtration. The solution is then diluted to 150 c.c., heated to

60—70°, and the copper and lead deposited electrolytically; with a current of 0·2—0·4 ampere and 2—3 volts, these metals are deposited within forty-five minutes, whilst the zinc remains in solution. The solution is next partly neutralised with solid potassium hydroxide, aluminium, zinc, and iron are precipitated by the addition of sodium carbonate, the precipitate is collected, washed with hot water, and dissolved in a very small quantity of dilute (1:4) sulphuric acid. The solution is treated with an excess of potassium hydroxide, and the clear liquid (except for a small precipitate of ferric hydroxide) measuring about 150 c.c. is submitted to electrolysis. The copper-coated cathode should be rotated at 600—800 revolutions per minute, and the current increased from 1 to 5 amperes in steps of 1 ampere every ten minutes. The zinc is deposited in forty minutes and, without interrupting the current, is washed, dried with alcohol, and weighed. The electrolyte contains the iron and aluminium, and these two metals are then separated in the usual way. W. P. S.

Sensitive Clinical Method for the Detection of Mercury in Urine. M. PERELSTEIN and J. ABELIN (*Chem. Zentr.*, 1915, ii. 1027; from *Münch. med. Woch.*, 1915, **62**, 1181—1183).—Five hundred c.c. of the urine are treated with 10 c.c. of concentrated hydrochloric acid, boiled for one minute, cooled, 6 c.c. of ammonia, 25 grams of sodium acetate, and 10 c.c. of 10% ferric chloride solution are added, and the mixture is again boiled. The precipitate formed is collected on a filter while the solution is still hot, washed with a small quantity of hot water, then dissolved in concentrated hydrochloric acid, and the mercury deposited on copper in the usual way. The deposited mercury may be identified by converting it into mercuric iodide. W. P. S.

Qualitative Analysis of the Iron Group in the Presence of Phosphates. ROBERT GILMOUR (*Chem. News*, 1916, **113**, 1—3; 13—15).—The solution, from which the metals of the silver and copper groups have been removed, is boiled to expel hydrogen sulphide, and the alkaline earths are precipitated as sulphates by means of sulphuric acid and alcohol. The precipitated sulphates are converted into carbonates and analysed according to a method described previously (A., 1915, ii, 486). The filtrate from the sulphates is evaporated to expel alcohol, sodium hydroxide is added, followed by an excess of sodium peroxide, the mixture is boiled for some minutes, and filtered. The filtrate contains aluminium, chromium and zinc, and most of the phosphate; the precipitate consists of hydroxides and phosphates of iron, nickel, cobalt, manganese, and magnesium. After the precipitate has been dissolved in hydrochloric acid, the solution is evaporated to dryness, the residue dissolved in water, and iron and phosphate separated by the basic acetate process. The filtrate from this precipitate contains nickel, cobalt, manganese, and magnesium; it is boiled, treated with hydrogen sulphide, and the nickel and cobalt sulphides are separated by filtration. The filtrate is rendered ammoniacal, the

manganese is separated as sulphide, and the magnesium subsequently as ammonium magnesium phosphate. W. P. S.

Rapid Estimation of Iron in Presence of Organic Substances F. FERRARI (*Ann. Chim. Applicata*, 1915, **4**, 341—343).—The preliminary destruction of the organic matter usually effected when iron is to be estimated in solutions containing hydroxylic organic acids, polyhydric alcohols, sugars, etc., may be avoided by the following method.

To the solution, which is made up to at least 150 c.c. and contains hydrochloric acid in excess (10·15 c.c. of the concentrated acid), chlorine water is added in small portions until a faint odour of the halogen persists. A cold, clear 6% solution of "cupferron" is then added drop by drop in amount at least one-fifth greater than that necessary for the complete precipitation of the iron, the liquid being kept in motion meanwhile. After fifteen to twenty minutes, when the pulverulent precipitate has mostly collected into large, friable, crystalline masses, these are broken up with a glass rod and the liquid filtered by aid of a filter pump, the suction, at first gentle, being continued until the precipitate is dry, when it is washed twice with cold water acidified with hydrochloric acid and afterwards with water alone until the filtrate loses its acidity; it is then treated several times with ammonia solution, and finally washed again with water. After thorough drying and cautious heating to redness in a covered platinum crucible, the precipitate is calcined in the air and the residual ferric oxide weighed. The whole of the operations require about one and a-half hours. The method gives exact results, but is not applicable in presence of copper, silver, lead, mercury, tin, bismuth, titanium, or zirconium, all these giving insoluble salts with "cupferron." T. H. P.

Separation and Estimation of Nickel. T. L. WALKER (*Trans. Roy. Soc. Canada*, 1915, [iii], **9**, 93—97).—The following method has been investigated for the separation of iron from nickel and cobalt: The hot solution containing iron, nickel, cobalt, copper, and lead chlorides is oxidised with a few drops of hydrogen peroxide in order to convert all the iron into the ferric condition. After nearly neutralising with sodium carbonate, red lead is added gradually to the boiling solution, until it is seen to be in excess by the distinct red colour of the precipitate, which is heavy and granular. The separation of the iron is complete in a few minutes. After collecting the precipitate, the lead and other metals are precipitated from the filtrate as sulphides, after which the fresh filtrate is concentrated to 100 c.c., 3 c.c. of concentrated sulphuric acid and 30 c.c. of strong ammonia added, and the nickel and cobalt deposited on a revolving cathode.

It is found that nickel and iron can be separated satisfactorily in this way, but not cobalt and iron, there being about a 10% loss with cobalt. Litharge does not give any better result with cobalt than does red lead.

Neumann's method (*Chem. Zeit.*, 1901, **25**, 731) for the separation of nickel from iron in steel and matte is found to be unsatisfactory.

Cobalt may be deposited successfully from chloride solutions under the following conditions: To the solution of cobalt chloride containing 0·13 gram of cobalt are added 3 c.c. of concentrated sulphuric acid, 30 c.c. of strong ammonia solution, and water to 150 c.c. Deposition is complete in twenty minutes at a revolving cathode, using 4 amps. and 5 volts.

The accuracy of the dimethylglyoxime method for nickel is about the same as the red lead method. T. S. P.

Rapid Analysis of Commercial Antimony Sulphide. A. Hutin (*Ann. Chim. anal.*, 1916, **21**, 3—7).—Moisture and calcium sulphate are estimated by the usual methods, and free sulphur by extracting the sample with acetone. Commercial antimony sulphide consists chiefly of a mixture of the tri- and penta-sulphides; these are converted into antimony tetroxide when ignited in the presence of mercuric oxide, and their quantity can be calculated from the weight of tetroxide obtained. The total quantity of antimony can also be estimated by reduction in a current of hydrogen. Samples which contain antimony tetroxide are not completely soluble in boiling hydrochloric acid. W. P. S.

Rapid Analysis of the So-called Antimony Glass. Jaroslav Milbauer (*Chem. Zeit.*, 1916, **40**, 108).—Antimony glass consists essentially of antimony oxide (90·5%) and antimony sulphide (8·7%), and these two constituents may be estimated as follows: 1 gram of the finely divided material is boiled for five minutes with 100 c.c. of dilute hydrochloric acid (1 : 4), the liquid is filtered through asbestos, the insoluble portion washed first with the dilute acid, then with water, dried, and weighed. The insoluble portion is now washed with a mixture of concentrated tartaric acid solution and dilute hydrochloric acid, and, after the total filtrate has been neutralised with sodium hydroxide, sodium hydrogen carbonate is added to the solution and the latter titrated with $N/10$-iodine solution. The result gives the quantity of antimony oxide present. The insoluble residue of antimony sulphide is then dissolved in concentrated hydrochloric acid, the solution boiled to expel hydrogen sulphide, and titrated with $N/10$-iodine solution under the same conditions. W. P. S.

Estimation of Titanium in Ferrotitanium. G. Röhl (*Chem. Zeit.*, 1916, **40**, 105—106).—Gooch's method, as modified by Thornton (A., 1912, ii, 1000) was found to yield concordant results, but these were lower by about 0·8% than those obtained by volumetric methods. Of the latter the methylene-blue process (A., 1913, ii, 1079; 1914, ii, 73) is rapid and accurate. W. P. S.

Estimation of Methyl Alcohol in Ethyl Alcohol. G. Reif (*Chem. Zentr.*, 1915, ii, 1056—1057; from *Arbeit. K. Gesundh.-Amt.*, 1915, **50**, 50—56).—The method depends on the fact that

methyl iodide reacts with methyl sulphide in the cold to form trimethylsulphonium iodide according to the equation: $MeI + SMe_2 = SMe_3I$, whilst the corresponding ethyl compound is not formed at the ordinary temperature if the quantity of methyl iodide in the mixture of methyl and ethyl iodides is not too small, but in this case its formation can be prevented by the addition of ether. The trimethylsulphonium iodide behaves as a salt of hydriodic acid, and can be estimated volumetrically. The mixture of the alkyl iodides is obtained as described by Wirthle (A., 1912, ii, 607), and the specific gravity of the mixture will indicate approximately the quantity of methyl iodide present. Two c.c. of the iodide mixture are placed in a 20 c.c. flask and, if the quantity of methyl iodide exceeds 5%, 2 c.c. of methyl sulphide are added; otherwise, only 1·5 c.c. of methyl sulphide and 0·5 c.c. of dry ether are added. The flask is closed, placed in a desiccator at 20° for twenty-four hours, the trimethylsulphonium iodide is then rinsed on to a dry filter with dry ether and washed with the same. The crystals are now dissolved in water and titrated with silver nitrate solution. One mol. of silver nitrate corresponds with 1 mol. of methyl alcohol. For the estimation of methyl alcohol in brandy a preliminary test is first made as described by Wirthle (*loc. cit.*) to detect the actual presence of this alcohol. One hundred c.c. of the sample are then treated with 10 c.c. of $N/1$-sodium hydroxide solution and distilled in an apparatus fitted with a Le Bel still-head, the quantity of distillate collected being 10 c.c. more than the amount of alcohol present. The quantity of total alcohol is now estimated in the distillate, and from the result is calculated the number of c.c. of the distillate corresponding with 10 c.c. of alcohol. This quantity of the distillate is used for the preparation of the mixed iodides; the boiling point observed during the distillation will indicate the proportion of methyl alcohol present, and, consequently, the quantities of iodine and phosphorus to be used, but an excess of 1 gram of iodine per 10 c.c. of the alcohols is without influence. When large quantities of methyl alcohol are present, it is recommended that the boiling point of the brandy should be closely observed so that a distillate containing approximately 10% of methyl alcohol may be obtained. The mixed iodides are then treated as above described. W. P. S.

Estimation of Methoxyl in Compounds Containing Sulphur. ALFRED KIRPAL and THEODOR BÜHN (*Monatsh.*, 1915, **36**, 853—863. Compare A., 1914, ii, 497).—The authors describe improvements in their modification of the Zeisel method for the estimation of methoxyl. They find that it is not necessary to use hydrogen, and that a current of carbon dioxide gives satisfactory results. The pyridine to absorb the methyl iodide is now enclosed in two small bubbling tubes wholly composed of glass, the only necessary connexion being for the attachment to the remainder of the apparatus. After evaporating off the pyridine in a dish, the remaining methiodide is dissolved in water and titrated with $N/10$ silver nitrate solution, using sodium chromate as an indicator.

With this modification of the Zeisel process there is no need for a pure hydriodic acid because the common impurities, for example, hydrogen sulphide and phosphine, do not affect the pyridine. The new method is also applicable to the estimation of the methylimide group, but is of no value for the estimation of ethoxyl, as ethyl iodide is only partly absorbed by the pyridine.

This method is also satisfactory for methoxyl estimations in sulphur compounds, but here the advantage over the Zeisel process is not so great as at first appears, because the latter can be made to give accurate results if the mixture of gas and vapour from the digestion flask is first passed through a slightly acidified solution of cadmium sulphate before reaching the silver nitrate solution. In this case any hydrogen sulphide is precipitated as cadmium sulphide. The unfavourable and inaccurate results obtained by Benedikt and Bamberger (A., 1891, 1296), who endeavoured to effect a similar result by the use of cadmium iodide solution, is explained by the fact that with this reagent the cadmium sulphide produced tends to remain in part in colloidal solution, in which form it is more active and reacts with the methyl iodide, giving methyl mercaptan. Experimental results are given indicating the applicability of the Zeisel method with the use of cadmium sulphate to the estimation of methoxyl and ethoxyl groups in compounds containing sulphur in various states of combination. D. F. T.

Detection of Glycerides by the Magenta–Sulphurous Acid Reagent. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1916, [vii], **13**, 65—77).—A modification of a test for glycerol described recently by François and Boismenu (A., 1915, ii, 110) may be used for the detection of glycerides in the presence of paraffins, waxes, resins, etc. The substance mixed with sand is heated in a test-tube for ten minutes nearly to redness, and the vapours produced are conducted into another test-tube containing a quantity of the magenta reagent (sulphurous acid, 220 c.c., 0·1% magenta solution, 30 c.c., and concentrated sulphuric acid, 3 c.c.); white fumes produced at the commencement of the heating should be prevented from coming into contact with the reagent by removing the source of heat for a few moments at a time. The test-tube containing the reagent is then heated in a boiling water-bath for fifteen minutes. If glycerides are present in the substance tested, the reagent is coloured red while cold, and the coloration changes to blue on heating; paraffins, waxes, resins, and caoutchouc yield vapours which give a red coloration with the cold reagent, but the latter becomes colourless when heated. The author also discusses the mechanism of the formation of the red and blue colorations. W. P. S.

Indirect Estimation of Sugars. G. ADANTI (*Boll. Chim. Farm.*, 1916, **55**, 33—35).—The method described by the author is identical with Bertrand's method (A., 1907, ii, 136).

T. H. P.

The Fehling-Soxhlet Method of Estimating Sugar. RUOSS (*Zeitsch. anal. Chem.*, 1916, **55**, 1—23).—The author gives

tables showing the quantities of sugar solutions (containing from 0·1 to 1% of reducing sugar) required to reduce 10 c.c. of Fehling's solution. In the titration of Fehling's solution with the sugar solution the end-point is found by filtering the solution after the bluish-green coloration has disappeared, acidifying the filtrate with acetic acid, and testing with potassium ferrocyanide solution. If a brown coloration is obtained, the titration is repeated, adding more of the sugar solution, until the filtered solution ceases to give a coloration with ferrocyanide. If the sugar solution contains nitrogenous substances the end-point is ascertained by acidifying the solution with acetic acid containing sodium chloride and adding a small quantity of potassium thiocyanate. The cuprous salt forms a precipitate, whilst any cupric salt remains in solution, and gives a coloration on the addition of ferrocyanide solution. In solutions containing from 0·01 to 0·1% of reducing sugar 10 mg. of sodium potassium tartrate should be added to the sugar solution in order to prevent the precipitation of cupric oxide from the Fehling's solution. Iodometric estimation of the excess of cupric salt remaining after Fehling's solution has been partly reduced by a sugar solution yields untrustworthy results owing to the action of oxidised sugar compounds on the liberated iodine. W. P. S.

Comparative Action of Sucrose and Invert-sugar on the Cupropotassic Solution. L. MAQUENNE (*Compt. rend.*, 1916, **162**, 145—149. Compare this vol., ii, 56).—A study of the variation of the reducing powers of invert-sugar and sucrose with variations in temperature and duration of heating. Starting from 70°, there is a very slight, steady rise in the reducing power of invert-sugar with rise in temperature, but for sucrose the increase is much more marked, particularly from 90° to 100°. Working with mixtures of these sugars the most satisfactory temperature is 70°, where, under the given conditions, the reducing power of invert-sugar is eight to ten thousand times greater than that of sucrose. For temperatures above 65° the time of heating has very little effect on the reducing power of invert-sugar, but in the case of sucrose the duration of heating has a very marked influence on the reducing power, which for temperatures in the neighbourhood of 70° is almost exactly proportional to the time of heating. W. G.

The Estimation of Reducing Sugars in the Presence of an Excess of Sucrose. L. MAQUENNE (*Compt. rend.*, 1916, **162**, 207—213. Compare Saillard, this vol., ii, 55).—The author has studied the effect of temperature and duration of heating on the estimation, his conclusions being in agreement with those of Saillard (*loc. cit.*). He has also examined the effect of varying the amount of sucrose present on the estimation of small quantities of reducing sugars. The results show that in the case of products poor in invert-sugar, 20 grams of sugar should be used when working with an external temperature of 65° or 100°, and 10 grams when working with boiling solutions, the total volumes of liquid used being 42·5 c.c. and 36·2 c.c. respectively. The method of estimation

should be adapted to the case under examination, using the method based on the separation of the cuprous oxide for products rich in invert-sugar, and the thiosulphate method for products poor in invert-sugar. It is necessary to carry out the reduction as soon as possible after the sugar is dissolved, and to titrate immediately after the reduction and cooling. W. G.

Use of Yeast for the Inversion of Sucrose and the Estimation of the Latter Polarimetrically or Chemically. H. PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1915, **33**, 29—30).—The addition of sodium salicylate prevents alcoholic fermentation when sucrose is inverted by yeast, and, since larger proportions of yeast may be used, the time required for the inversion is shortened. The results obtained in the estimation of sucrose in molasses when the sugar has been inverted with yeast treated with sodium salicylate agree with those found by the ordinary inversion method. W. P. S.

Preparation of Very Active Salicylated Yeast for the Inversion of Sucrose. H. PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1915, **33**, 30—33).—Yeast is liquefied immediately when treated with 7% of its weight of sodium salicylate; the solution thus obtained retains its activity (inverting power on sucrose) for several months, and a quantity of it corresponding with 3 grams of yeast is capable of inverting 3·5 grams of sucrose within twenty minutes. W. P. S.

Use of Different Substances in the Preparation of Invertase Solution. Possible Sources of Error. H. PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1915, **33**, 33—34).—Thymol, chloroform, and formaldehyde have been used in the preparation of invertase solution from brewers' yeast; whilst the former is optically inactive and does not reduce Fehling's solution, the last two, in dilute solution, although optically inactive, reduce Fehling's solution. An error may, therefore, be introduced in the estimation of the cupric-reducing power of sugar solutions to which invertase solution containing either of these substances has been added. Sodium salicylate is to be preferred to any of the above substances in the preparation of invertase solutions. W. P. S.

Estimation of Raffinose by Means of Different Yeasts. H. PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1915, **33**, 41).—The different actions of top and bottom fermentation yeasts on raffinose noted by Hudson (A., 1914, i, 1147) have been investigated by the author and found to be as stated; the method of estimating raffinose described by Hudson and Harding (A., 1915, ii, 803) may be used for the analysis of molasses containing a small quantity of raffinose. It is mentioned that 1 gram of anhydrous raffinose, when inverted with hydrochloric acid, yields 0·765 gram of reducing sugar; inverted with top fermentation yeast it gives 0·745 gram, and with bottom fermentation yeast, 0·965 gram of reducing sugar, all expressed in terms of invert-sugar. W. P. S.

Detection of Small Quantities of Oxalic Acid in Wine. HANS KREIS and W. I. BARAGIOLA (*Chem. Zentr.*, 1915, ii, 810—811; from *Schweiz. Apoth. Zeit.*, 1915, **53**, 397—400).—Oxalic acid is added occasionally to wine to decrease the quantity of calcium salts present and to increase the "residual acidity"; even when the quantity of oxalic acid added is insufficient to precipitate the whole of the calcium a small quantity of oxalic acid remains in solution owing to the solubility of calcium oxalate in the presence of tartaric acid. To detect a small quantity of oxalic acid in wine, 50 c.c. of the sample are heated to boiling, 3 c.c. of 5% calcium chloride solution are added, and the mixture is rendered ammoniacal; acetic acid is now added to the hot solution until the latter is just acid in reaction (an excess of acid must be avoided), the mixture is cooled, submitted to centrifugal action, and the sediment examined under the microscope. Characteristic crystals of calcium oxalate will be observed if the wine contained as little as 0·02 gram of oxalic acid per litre. Still smaller quantities (0·01 gram per litre) of oxalic acid may be detected by treating 50 c.c. of the wine (cold) with 2·5 c.c. of 5% calcium chloride solution, 2·5 c.c. of acetic acid, and 5 c.c. of saturated sodium acetate solution. After twenty-four hours, the mixture is shaken in order to disturb the sediment of calcium oxalate (if present); the greater part of the precipitated calcium tartrate adheres to the bottom of the vessel. The liquid is now submitted to centrifugal action, the sediment transferred to a small, drawn-out tube, again submitted to centrifugal action, and examined microscopically. The calcium oxalate contained in the cell tissue of grapes does not find its way into the must or wine. W. P. S.

Acidimetric Estimation of Oxalic Acid, Using Methyl-orange as Indicator, and its Estimation by the Iodide-Iodate Method. G. BRUHNS (*Zeitsch. anal. Chem.*, 1916, **55**, 23—51).—Oxalic acid may be titrated accurately with alkali solutions, using methyl-orange as indicator, provided that an equivalent quantity of calcium chloride solution is added when the acid has been almost completely neutralised. Without the addition of calcium chloride the end-point of the titration is not sharp owing to the tendency of the added alkali to form hydrogen salts with the acid. The iodide–iodate method is not satisfactory when applied to oxalic acid; the liberation of iodine is extremely slow towards the end of the reaction, and, if calcium chloride is added, the results obtained are slightly too low. W. P. S.

Modification of the So-called Mohler's Reaction for Benzoic Acid. J. GROSSFIELD (*Chem. Zentr.*, 1915, ii, 1313—1314; from *Zeitsch. Nahr. Genussm.*, 1915, **30**, 271—273).—Von der Heide and Jacob's method (A., 1910, ii, 359) of carrying out Mohler's test (compare Robin, A., 1908, ii, 1078) is trustworthy but somewhat tedious, and the reduction of the dinitrobenzoic acid with ammonium sulphide has little advantage. The author modifies the method as follows: The dry alkali benzoate residue is mixed with 0·1 gram

of potassium nitrate and 1 c.c. of concentrated sulphuric acid, the mixture is heated for twenty minutes on a boiling water-bath, then cooled, diluted with 2 c.c. of water, again cooled, and treated with 10 c.c. of 15% ammonia and 2 c.c. of 2% hydroxylamine hydrochloride solution. A red coloration develops more or less rapidly according to the amount of benzoic acid present; the coloration develops more quickly if the mixture is heated, and reaches its greatest intensity when the mixture is cooled. In the colorimetric estimation a standard iron solution (containing 1 mg. of Fe_2O_3 per c.c.) mixed with thiocyanate solution may be used for the comparison. W. P. S.

Analysis of Medicated Drinks. B. H. St. John (*J. Soc. Chem. Ind.*, 1916, **35**, 68—69; from *J. Assoc. Off. Agric. Chem.*, 1915, **1**, 343—345).—The acidified sample is extracted with a mixture of chloroform and alcohol, and the acids present are transferred to aqueous solution by washing the extract with sodium carbonate solution. Caffeine if present is then estimated by evaporating the washed chloroform solution to dryness. In the sodium carbonate extract, salicylic acid is estimated by adding an excess of iodine, and after warming for an hour, collecting, and weighing the precipitate; its weight, multiplied by 0·4657, gives the amount of sodium salicylate present. "Saccharin" and benzoic acid, which are also present in the sodium carbonate extract, are estimated, the one by conversion into its silver salt and the other by steam distillation. Phosphoric acid is precipitated directly from the beverage as ammonium magnesium phosphate, which is converted into phosphomolybdate, and back again to ammonium magnesium phosphate, and weighed as pyrophosphate. Glycerol is estimated by the American official method for the estimation of this substance in wines, but since the residue of glycerol obtained may contain caffeine and other substances, it is oxidised with permanganate and the glycerol calculated from the amount of oxalic acid produced. G. F. M.

Melting Point of Salicylic Acid, and a Test for the Presence of *p*-Hydroxybenzoic Acid. Henry L. Smith (*Analyst*, 1916, **41**, 3—5).—Salicylic acid prepared from different sources and dried over sulphuric acid under reduced pressure had m. p. 158·5°; *p*-hydroxybenzoic acid melted at 213·5°, the same melting point being obtained after crystallisation and drying over sulphuric acid. For the detection of *p*-hydroxybenzoic acid in salicylic acid, the formation of basic calcium salicylate, which is less soluble than the calcium salt of *p*-hydroxybenzoic acid, may be employed to concentrate the latter acid. The salicylic acid to be tested is mixed with an excess of calcium hydroxide and water, evaporated to dryness, and the residue extracted with water. The aqueous extract is acidified, extracted with ether, and the ethereal extract evaporated. When an ethereal solution of this residue is allowed to evaporate on a microscope slide, the *p*-hydroxybenzoic acid crys-

tallises in tufts which are quite different in appearance from the crystals of salicylic acid seen at the same time. W. P. S.

New Reaction of Picric Acid and its Application. J. CASTETS (*J. Pharm. Chim.*, 1916, [vii], **13**, 46—49).—The reaction depends on the formation of 2-bromo-4 : 6-dinitrophenol and the red coloration which this substance gives with ammonia vapour or potassium cyanide. A solution containing picric acid is treated with bromine water, heated to boiling, cooled, and extracted with ether. The ethereal solution is separated and divided into two portions, one of which is evaporated, and the residue treated with ammonia vapour; a red coloration is obtained which is destroyed by an excess of ammonia or by the addition of water. The other portion is evaporated drop by drop on a piece of filter paper; a red coloration is obtained if the paper is then treated with ammonia vapour, or with a drop of potassium cyanide solution and again dried. For the detection of picric acid in urine 100 c.c. of the sample are acidified with 2 c.c. of hydrochloric acid, and extracted with chloroform. The chloroform solution is evaporated, the residue dissolved in water, treated with bromine, and the test carried out as described. In the case of beer, the liquid is evaporated, the residue treated with alcohol for twelve hours, the alcoholic solution then decanted, filtered, evaporated, the residue dissolved in water, the solution acidified, and treated as described for urine. The test will detect the presence of 5 mg. of picric acid per litre of urine. W. P. S.

Estimation of Uric Acid in Blood. CARL MAASE and HERMANN ZONDEK (*Chem. Zentr.*, 1915, ii, 858—859; from *Münch. med. Woch.*, 1915, **62**, 1110—1111).—Five c.c. of the blood are boiled with the addition of 25 c.c. of $N/100$-acetic acid, the hot mixture is filtered, the coagulum is washed with 60 c.c. of boiling water containing 0·5 gram of sodium acetate, the filtrate is acidified with 2·5 c.c. of 50% acetic acid, and evaporated to a volume of 5 c.c. This residual solution is neutralised with sodium carbonate solution, transferred to a flask, 2·5 c.c. of saturated sodium carbonate solution and 1 c.c. of Autenrieth's phosphotungstic acid reagent are added, the mixture is diluted to 25 c.c., and, after ten minutes, the coloration is compared with a standard scale in the Autenrieth-Konigsberger colorimeter (A., 1910, ii, 910). To correct for the influence of other blood constituents (tyrosine and peptone) 0·5 mg. is deducted from the result obtained. W. P. S.

Sensitive Method for the Examination of Oils. A. MAZZARON (*Chem. Zentr.*, 1915, ii, 1316—1317; from *Staz. sperim. agrar. ital.*, 1915, **48**, 583—594).—The method depends on the measurement of the quantity of sulphur dioxide evolved when an oil is treated with concentrated sulphuric acid. Twenty c.c. of the oil are placed in a flask connected with an absorption vessel containing a definite quantity of $N/10$-iodine solution and 5 c.c. of sulphuric acid (D 1·8417) are added to the oil. A current of air is drawn

through the apparatus, the mixture in the flask is shaken for fifteen seconds, and the current of air continued until all the sulphur dioxide has been absorbed by the iodine; the excess of iodine is then titrated with thiosulphate solution. The reaction should be carried out at a temperature of 20°. The number of c.c. of $N/10$-iodine solution required to oxidise the sulphur dioxide evolved from 20 c.c. of an oil is termed the sulphur dioxide number of the oil. This number for various oils was found to be as follows: Olive oil, 2·4; sesame oil, 49·5; cottonseed oil, 137·5; maize oil, 65; soja-bean oil, 223; rape oil, 15; earthnut oil, 7. There does not appear to be any definite relation between the sulphur dioxide number and the sulphuric acid thermal number of the oils. W. P. S.

Estimation of Fat (in Animal Substances, etc.). HELMAN ROSENTHAL and P. F. TROWBRIDGE (*J. Biol. Chem.*, 1915, **20**, 711—717).—Whilst Soxhlet's method (simple extraction with ether) yields trustworthy results in the case of such substances as pork fat, where the fat is the only soluble substance present, it is not trustworthy for the estimation of fat in blood, liver, etc., and, for the latter purpose, the authors prefer the following modification of a method proposed by Liebermann and Szekely (A., 1898, ii, 655). The sample (20 grams of blood or 10 grams of liver) is heated on a water-bath for two hours with 30 c.c. of 20% sodium hydroxide solution, the warm solution then transferred to a separating funnel, acidified with 35 c.c. of 20% hydrochloric acid (D 1·1), cooled, and extracted with ether. The ethereal solutions are evaporated, the residue is dissolved in about 25 c.c. of light petroleum (b. p. 30—50°), 15 c.c. of 95% alcohol are added, and the solution is titrated with $N/20$-alkali solution, using phenolphthalein as indicator. The result is calculated into neutral glyceride. The authors also prefer this method to that of Kumagawa and Suto (A., 1908, ii, 331), as in the latter there seem to be many possibilities of error in the separation of the unsaponifiable substances.

W. P. S.

Estimation of Formaldehyde in the Presence of Acetone. J. BOES and H. WEYLAND (*Chem. Zentr.*, 1915, ii, 982—983; from *Hyg. Rundschau*, 1915, **25**, 657—663).—A definite quantity of the formaldehyde solution containing acetone is treated in a stoppered flask with an excess of neutralised ammonium chloride solution; litmus solution is added, followed by an excess of $N/1$-sodium hydroxide solution, and, after one hour, the mixture is titrated with $N/1$-acid. The reaction proceeds according to the equation: $4NH_4Cl + 6CH_2O + 4NaOH = C_6H_{12}N_4 + 4NaCl + 10H_2O$.

W. P. S.

Analysis of Vanillin. J. F. SACHER (*Chem. Zentr.*, 1915, ii, 1027; from *Deutsch. Parfumerie Zeit.*, 1915, **1**, 187—188).—The method proposed depends on the fact that vanillin in alcoholic solution can be titrated with $N/10$-sodium hydroxide solution, using

phenolphthalein as indicator; the end-point of the titration is sharp. The result of the titration will indicate whether or not small quantities of foreign substances are present. W. P. S.

Significance of the Strophanthin Reaction which is Obtained by the Action of Sulphuric Acid on Strophanthus Seeds. ALESSANDRO BALDONI (*Chem. Zentr.*, 1915, ii, 984—985; from *Arch. Farmacol. sperim.*, 1915, **19**, 511—528).—Fresh strophanthus seeds (St. Kombé) give a green coloration when treated with concentrated sulphuric acid, but the reaction is not obtained with old seeds. In some cases where a reaction is not obtained with the concentrated acid a coloration is given when 80% acid is used; 50% sulphuric acid never yields a reaction. Exposure of the seeds to sunlight causes a decrease in the intensity of the coloration. The substance in the seeds which gives the reaction can be extracted partly by means of ether or 95% alcohol, but not by light petroleum. Although the reaction will not distinguish between the various strophanthins, it is useful in conjunction with other tests.
W. P. S.

Estimation of Urea and Extractives in Urine by the Xanthhydrol Method. L. MAESTRO (*Chem. Zentr.*, 1915, ii, 984; from *Arch. Farmacol. sperim.*, 1915, **19**, 572—576).—A modification of this method (A., 1914, ii, 506, 593) is described. One c.c. of the urine is mixed with 9 c.c. of water and 20 c.c. of glacial acetic acid, and 5 c.c. of a 6% solution of xanthhydrol in glacial acetic acid are added in five equal portions at intervals of ten minutes. After one hour the precipitate is collected, washed with methyl alcohol, dried, and weighed; its weight multiplied by 142·857 gives the quantity of urea per litre of the urine. The extractives may be estimated in the filtrate. W. P. S.

Purification of the Residues of the Ether and Chloroform Extracts in the Forensic Detection of the Alkaloids. A. CARDOSO PEREIRA (*Chem. Zeit.*, 1916, **40**, 39).—The residues from the ethereal or chloroform extracts in forensic analysis may be completely freed from ptomaines by boiling the original tartaric acid extract, after extraction with ether, with a few c.c. of perhydrol for a few minutes, and then proceeding with the analysis in the usual way. Strychnine, nicotine, and coniine are unaffected by this treatment, but morphine is converted into oxidation products. G. F. M.

Estimation of Caffeine in Coffee. G. FENDLER and W. STÜBER (*Chem. Zentr.*, 1915, ii, 1315; from *Zeitsch. Nahr. Genussm.*, 1915, **30**, 274—277. Compare A., 1914, ii, 757).—A method described by Burmann (A., 1910, ii, 465) was found to be untrustworthy.
W. P. S.

Detection of Safflower in Saffron. G. VICARI (*Chem. Zentr.*, 1915, ii, 1318; from *Mitt. Lebensmittelunters. Hyg.*, 1915, **6**, 195—197).—The phosphomolybdic acid test described by Verda (A.,

1914, ii, 305) is useful for the detection of safflower (*Carthamus tinctorius*) in saffron; the latter gives a blue coloration, whilst safflower yields a red coloration. W. P. S.

Distinction between Erythrosin and Rose-Bengal. Estimation of their Commercial Value. ALEXANDRE LEYS (*Ann. Chim. anal.*, 1916, **21**, 25—32).—Erythrosin, the sodium salt of tetraiodofluorescein, contains 57·7% of iodine, and is free from chlorine; its solutions are practically free from fluorescence. It is, however, rarely met with in a pure state in commerce, a portion of the iodine being replaced by chlorine; these mixed halogen compounds may exhibit fluorescence, particularly when the halogens are attached to both the phthalic and resorcinol nuclei. Rose-bengal, the sodium salt of tetraiododichlorofluorescein, contains 53·53% of iodine and 7·48% of chlorine, and is less valuable than erythrosin. Estimations of the iodine and of the ratio of iodine to chlorine in a sample will give information as to whether it is pure erythrosin. The material should be extracted with alcohol to separate mineral substances, the alcoholic solution then evaporated, and the residue dried at 100°. A weighed portion of this residue is fused with a mixture of potassium hydroxide and sodium carbonate, cooled, dissolved in water, and an aliquot portion of the solution titrated in the usual way with silver nitrate solution; the iodine is then estimated in another portion of the solution, the potassium nitrite method being used for the purpose. W. P. S.

Simple Apparatus for the Estimation of Small Quantities of Albumin. RICHARD WEISS (*Chem. Zentr.*, 1915, ii, 811—812; from *Münch. med. Woch.*, 1915, **62**, 1010).—Five c.c. of phosphotungstic acid reagent (phosphotungstic acid, 1·5 gram; hydrochloric acid, 5 c.c.; and 95% alcohol, 95 c.c.) are placed in a specially constructed albuminometer, and filtered urine is added until a distinct turbidity is produced. The reagent will give a turbidity with as little as 0·0001 gram of albumin, and the quantity of urine added to produce a turbidity will, consequently, contain this amount of albumin. The apparatus is graduated so that the quantity of urine used may be noted. W. P. S.

Estimation of Albumin in Urine. W. AUTENRIETH and FRIEDA MINK (*Chem. Zentr.*, 1915, ii, 1265; from *Münch. med. Woch.*, 1915, **62**, 1417—1421).—A colorimetric method, based on the biuret reaction, is described; the albumin is first precipitated by warming the urine with the addition of acetic acid. The Autenrieth-Koenigsberger colorimeter (A., 1910, ii, 910) is used for comparing the colorations obtained. W. P. S.

Rapid Methods for the Estimation of Albumin and Sugar in Urine. EMIL LENK (*Chem. Zentr.*, 1915, ii, 1265; from *Deutsch. med. Woch.*, 1915, **41**, 1281).—For the estimation of albumin, the urine is diluted so that it contains not more than 0·4% of albumin, and is filled into an Esbach tube up to the mark

U; Esbach's reagent is then added up to the mark *R*, a small quantity of powdered pumice-stone is introduced, the tube is closed, and inverted about ten times, but not shaken. The mixture becomes clear within two minutes, and the estimation can be completed in ten minutes. Sugar is estimated by titration against Fehling's solution, potassium ferrocyanide solution acidified with acetic acid being used as an external indicator in determining the end-point of the titration. W. P. S.

Test for Urobilin in Urine and Fæces. ADOLF EDELMANN (*Chem. Zentr.*, 1915, ii, 1059; from *Wien. klin. Woch.*, 1915, **28**, 978—979).—The test depends on the formation of a red compound when urobilin is treated with mercuric chloride. Five c.c. of a 10% alcoholic mercuric chloride solution are added to 10 c.c. of the urine and the mixture is shaken with amyl alcohol; the amyl alcohol layer is then transferred to a test-tube and mixed with a few c.c. of clear, filtered, 10% alcoholic zinc chloride solution. If large quantities of urobilin are present, the amyl alcohol solution will exhibit a red colour, and a green fluorescence appears on the addition of the zinc chloride; with a small quantity of urobilin, the green fluorescence is seen only when a ray of light is projected through the clear liquid. The reaction is not affected by any of the other constituents of normal or pathological urine. For the detection of urobilin in fæces a few grams of the latter are mixed with a very small quantity of water, an excess of alcoholic mercuric chloride solution is added, the mixture filtered, and the filtrate is treated with a few c.c. of alcoholic zinc chloride solution; a green fluorescence is seen if urobilin is present. W. P. S.

Detection of Bile in Soaps. F. STEINITZER (*Chem. Zentr.*, 1915, ii, 810; from *Chem. Rev. Fett. Harz-Ind.*, 1915, **22**, 69—70). —Five grams of the soap are dissolved in hot water, the solution is filtered, and the filtrate treated with dilute sulphuric acid. After cooling, the cake of fatty acids is separated, dried between filter-paper, then heated at 70° in a test-tube with 10 c.c. of sulphuric acid (1 : 1), and the hot mixture treated with a few drops of 10% sucrose solution. If biliary acids are present, a red to violet-red coloration develops on keeping the mixture at 70° for a few minutes (Pettenkofer's reaction). W. P. S.

General and Physical Chemistry.

Atomic Refraction of Phosphorus in Certain Organic Phosphorus Compounds. A. E. ARBUZOV and A. A. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2015—2027).—The results obtained by Zecchini (A., 1893, ii, 353, 354; 1894, ii, 221) and by Kovalevski (*J. Russ. Phys. Chem. Soc.*, 1897, **29**, 217) are discussed. In the authors' measurements the index of refraction was determined at 20° for the D, H_α, H_β, and H_γ lines, and the values of $M(n^2-1)/D_4^{20}(n^2+2)$ calculated. The values of the atomic refraction of phosphorus are given for the D line (1) according to Conradi; with the three compounds containing quinquevalent phosphorus the values are calculated also on the assumption that all the oxygen is singly linked to the phosphorus; (2) according to Traube. The results are as follows:

Compound.	Line.	$\frac{M(n^2-1)}{D(n^2+2)}$.	Atomic refraction of phosphorus (D). Conradi.	Traube.
$P(OEt)_3$	D	42·78		
	H_α	42·57	7·45	7·12
	H_β	43·33		
	H_γ	43·79		
$POEt(OEt)_2$	D	40·67	For O′	
	H_α	40·50	5·34	5·01
	H_β	41·08	For O″	
	H_γ	41·43	4·57	
$POH(OEt)_2$	D	31·75	For O′	
	H_α	31·61	5·62	5·47
	H_β	32·08	For O″	
	H_γ	32·35	4·86	
$PO(OEt)_3$	D	41·90	For O′	
	H_α	41·74	5·05	4·64
	H_β	42·32	For O″	
	H_γ	42·66	4·28	

For the atomic refraction of phosphorus for the D line, calculated according to the Lorenz and Lorentz formula, Kovalevski (*loc. cit.*) found: from $PCl_2{\cdot}OMe$, 7·72; $PCl_2{\cdot}OEt$, 8·22; $PCl_2{\cdot}OPr$, 8·01; $PCl_2{\cdot}O{\cdot}C_4H_9$, 8·04; and $PCl_2{\cdot}O{\cdot}C_5H_{11}$, 7·60. The atomic refraction calculated from Zecchini's results for a compound regarded by this author as $P(OEt)_3$ is 2·97; according to Arbuzov's results (A., 1907, i, 8, 174, 275), this compound is probably impure diethylphosphorous acid, $OH{\cdot}P(OEt)_2$, and recalculation of Zecchini's result on this assumption gives the value 4·96 for the atomic refraction, this number agreeing well with the author's value, 4·86.

For the four compounds of the table given above, the authors have determined the values of $D_4^{b.p.}$, the molecular volume, and the atomic volume of phosphorus according to Kopp's data; the last of these magnitudes has the values 32·25, 26·55, 27·38, and 32·79 for $P(OEt)_3$, $POEt(OEt)_2$, $POH(OEt)_2$, and $PO(OEt)_3$ respectively

For the same four compounds, the ratio of the molecular volume to the molecular refraction for the D line has the values 4·77, 4·88, 4·89, and 5·07, the mean being 4·9. Further, the ratios of (1) the molecular volumes, and (2) the molecular refractions are: for $P(OEt)_3/POEt(OEt)_2$, (1) 1·03, (2) 1·05; for $P(OEt)_3/POH(OEt)_2$, (1) 1·31, (2) 1·35; and for $P(OEt)_3/PO(OEt)_3$, (1) 0·96, (2) 1·02. The ratios 1·03 : 1·05, 1·31 : 1·35, and 0·96 : 1·02 have the approximately equal values 0·98, 0·97, and 0·94.

T. H. P.

The Neutral Atom and the Positive Ion as Carriers of the Band Spectrum and of the Series Spectrum of Hydrogen. J. STARK (*Ann. Physik*, 1916, [iv], **49**, 179—200).—The conditions under which the many-lined (band) and the series spectra of hydrogen are emitted lead to the view that the series spectrum is emitted by positively charged hydrogen ions and the band spectrum by neutral hydrogen atoms. The fact that the lines of the band spectrum show no appreciable canal ray Doppler effect affords evidence that high-speed neutral atoms are not present in any measurable quantity in hydrogen canal rays. It is probable that these lines are emitted as a result of collisions with the canal rays.

H. M. D.

The Single-line Spectra of Magnesium and other Metals and their Ionising Potentials. J. C. MCLENNAN (*J. Franklin Inst.*, 1916, **181**, 191—207.* Compare A., 1915, ii, 657).—Previous experiments have shown that the vapours of mercury, cadmium, and zinc give rise to spectra which consist of a single line when the heated vapours are bombarded by electrons the energy of which lies within certain well-defined limits. It has now been found that magnesium vapour behaves similarly, the wave-length of the single-line emission being λ 2852·22.

The wave-lengths of the single-lines in the emission spectra of mercury, cadmium, and zinc have been found to be identical with those of bands in the corresponding absorption spectra, and this relation is also shown by magnesium, the absorption spectrum of which contains bands at λ 2852·22 and λ 2073·36. Since these lines are the first members of Paschen's combination series, $\nu = 2{,}p_2 - m{,}S$ and $\nu = 1{\cdot}5{,}S - m{,}P$ respectively, it follows that the absorption spectrum of magnesium is analogous to the spectra of the vapours of mercury, cadmium, and zinc.

On the assumption that this analogy extends to calcium, strontium, and barium and thallium, it is calculated that the single-line emission spectra, which would be emitted by these vapours when suitably bombarded by electrons, should have the wave-lengths λ 4226·91, λ 4607·52, λ 5535·69, and λ 5350·65 respectively.

According to Franck and Hertz (*Ber. Deut. physikal. Ges.*, 1914, **11**, 512), the single-line frequency of mercury is identical with that calculated from the minimum ionising potential on the basis of the quantum theory. By the same method the author has calculated the minimum ionising potentials of all the metals referred to above.

* and *Proc. Roy. Soc.*, 1916, [A], **92**, 305—312.

It is considered, however, that this method of correlating single-line frequencies with minimum ionising potentials is difficult to reconcile with Bohr's theory. H. M. D.

A Comparison of the Arc and Spark Spectra of Nickel Produced under Pressure. E. G. BILHAM (*Phil. Mag.*, 1916, [vi], **31**, 163—170).—According to Duffield (A., 1915, ii, 658), the displacements per atmosphere of reversed nickel lines are greater for the arc spectrum than for the spark spectrum. In view of the fact that the pressure of 10 atmospheres which were employed in the author's observations on the spark spectrum coincides with a region in which Duffield's observations on the arc spectrum show an abnormally high rate of shift per atmosphere, it has been considered advisable to subject the data to a more rigorous comparison. The conclusion reached is that the behaviour of lines easily reversed, or tending towards reversal, is approximately the same for both arc and spark lines. Differences are shown, on the other hand, by unreversed lines. This result is exactly the opposite of that reached by Duffield in his analysis of the data. H. M. D.

The High Frequency Spectra of the Elements from Gold to Uranium. MANNE SIEGBAHN and EINAR FRIMAN (*Physikal. Zeitsch.*, 1916, **17**, 17—18 *).—Measurements have been made of the wavelengths of the stronger α-line in the X-ray spectra of the elements gold, mercury, thallium, lead, bismuth, thorium, and uranium. The relation between the atomic number and the square root of the frequency is found to be linear, as required by Moseley's formula, if the atomic numbers assigned to thorium and uranium are 90 and 92 respectively. H. M. D.

Absorption Spectra of the Vapours of Inorganic Salts. E. J. EVANS (*Phil. Mag.*, 1916, [vi], **31**, 55—62).—The examination of the absorption spectra of the vapours of ammonium chloride, mercuric and mercurous chloride, cadmium chloride, bromide, and iodide has shown that the vapours have no well-defined absorption lines or bands in the region λ 2500 to λ 6700. With the possible exception of ammonium chloride, the salts show general selective absorption in the ultraviolet, which in the case of the cadmium salts is greater for the iodide and bromide than for the chloride.

H. M. D.

The Rotation Dispersion of Hydrogen. PAUL SCHERRER (*Physikal. Zeitsch.*, 1916, **17**, 18—21).—A theoretical paper, in which it is shown that the observed rotation of the plane of polarisation exhibited by hydrogen in a magnetic field can be calculated on the assumption that the changes produced in the interior of the atom by the application of the magnetic field are in accordance with the requirements of Newtonian mechanics. H. M. D.

The Magnetic Rotation of the Plane of Polarisation in Titanium Tetrachloride. II. L. H. SIERTSEMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 925—932. Compare A., 1915, ii,

* and *Phil. Mag.*, 1916, [vi], **31**, 403—406.

610).—The experimental observations on the magnetic rotatory dispersion of titanium tetrachloride are shown to be in agreement with the requirements of Lorentz's theory. H. M. D.

The Life of Radium. ELLEN GLEDITSCH (*Amer. J. Sci.*, 1916, [iv], **41**, 112—124).—Boltwood's method of finding the period of radium, by separating the whole of the ionium present in a uranium mineral and determining the rate of growth of the radium from it in terms of the equilibrium amount of radium in the mineral, has been repeated. In the first place a solution more than six years old, prepared by Boltwood, was found to be generating radium at the same rate as it had done six years previously, showing that the rate of change of ionium is very small. Four minerals were used: (1) Uraninite, N. Carolina, containing 69·4% uranium, very pure and free from alteration products. (2) Cleveite, from Saetersdalen, Norway, containing 10% of rare earths. (3) Bröggerite, Raade, Norway; (4) the same, a very pure specimen. The ionium was removed from the solution by precipitating rare earths, mostly thorium, by oxalic acid in (1); by means of hydrofluoric acid in (2); by oxalic acid and thorium in (3); and by rare earths and hydrofluoric acid in (4). Several successive precipitations were employed, the final being kept separately as a test solution, so that if no radium were generated in it, all the ionium must have been removed in the previous precipitations. The values for the radioactive constant, $\lambda(\text{year})^{-1}$, and for the half-period of radium from these four preparations are shown below:

	I.	II.	III.	IV.
$\lambda \times 10^4$	3·71	3·90	4·22	4·14
Half period (years)......	1865	1777	1642	1774

The last two results are considered the most satisfactory, I being a preliminary test, and II being slightly uncertain on account of an accident. The mean of III and IV, 1660 years, agrees excellently with Rutherford's value, 1690 years, deduced from his experiments with Geiger on the counting of the number of α-particles emitted per second per gram of radium. F. S.

The Laws of Radioactive Transformation. A. DEBIERNE (*Ann. Physique*, 1916, [ix], **4**, 309—322).—The general equation of radioactive change, $dn_2 = \lambda_1 n_1 dt - \lambda_2 n_2 dt$, where n_1 and n_2 are the numbers of atoms of any two successive products of radioactive constants λ_1 and λ_2, and the usual resulting integrations are considered from a fresh point of view, in which each atom is regarded as spending times, t_1, t_2, t_3 . . . in the successive forms A, B, C . . . A so-called "equation of destiny" is so obtained which permits the various problems of radioactive change to be treated generally in a simple manner. F. S.

Considerations on the Mechanism of Radioactive Changes and the Constitution of Atoms. A. DEBIERNE (*Ann. Physique*, 1916, [ix], **4**, 323—345).—It is supposed that in each atom there exists an element of internal disorder. In the law of

a unimolecular chemical change, which is formally that of radioactive change, the element of disorder is sought in thermal agitation. In radioactive change there is supposed to be something analogous, in the interior of the atom, to the decoordinated motion of the molecules of a gas. This idea is discussed generally at considerable length. F. S.

The Distribution of the Active Deposit of Thorium in an Electric Field. G. H. HENDERSON (*Trans. Nova Scotian Inst. Sci.*, 1914–1915, **14**, 1—16).—A convenient form of apparatus for the investigation of the distribution of residual atoms in an electric field is described. Observations made with thorium in dry air show that the percentage cathode activity increases with the applied potential, the curve expressing the relation having a close resemblance to the ionisation saturation curve. With an applied potential of 12,000 volts the cathode activity is 100% within the limits of experimental error, and there is no evidence of the existence of neutral residual atoms.

In ethyl ether vapour, on the other hand, the whole of the residual thorium atoms are initially uncharged. In mixtures of ether vapour and air the proportion of charged atoms depends on the composition of the gas. A similar variation is indicated by the results obtained in experiments with moist air. H. M. D.

The Branching Point of the Thorium Series. STANISLAW LORIA (*Physikal. Zeitsch.*, 1916, **17**, 6—9).—The result of Barratt and Wood (A., 1914, ii, 606) puts in doubt the generally accepted scheme of disintegration of the thorium series and the position of the branching point, and their explanation and scheme are contrary to the Soddy-Russel-Fajans generalisation. The result has been confirmed, but the explanation has been shown to be untenable. A well-marked inflection in the curve connecting the volatility of thorium $B+C$ with temperature occurs at 920°, when some 35% has been volatilised. An identical behaviour is shown, however, by the radium-C curve. Since here the proportion between the two branches is 0·03 : 99·97, it follows that the explanation advanced as to the inflection at 35% in the case of thorium, namely, that the number giving 35% of the α-rays of thorium-C is a distinct substance, so that the branching must occur before its formation, does not explain the inflection. The cause of this is regarded as of chemical rather than radioactive origin, and possibly is due to the formation of several oxides of thorium-C, analogous to those of the isotope bismuth, only stable within certain ranges of temperature. There is a difference in the volatility curves, the same for both thorium-C and radium-C, according as the active deposit is obtained directly or by electrolysis, which may be due to formation of alloys with the supporting metal. This view is being further tested. F. S.

The Question of Isotopic Elements. II. K. FAJANS (*Physikal. Zeitsch.*, 1916, **17**, 1—4).—The author now agrees with Hevesy and Paneth in their point of view as regards the potential of a

metal immersed in a solution of its isotope, but, regarding this as merely a special electrochemical problem, proceeds to criticise the general view of isotopes taken by these authors. The chief subject discussed is whether the interpretation of Hevesy and Paneth with regard to their electrochemical experiments is "new," or differs merely as to expression from the practice, "as old as the establishment of the existence of chemically inseparable elements," of regarding a mixture of isotopes as one element, which has been repeatedly applied by the author in describing precipitation experiments. Only in the case of a metal immersed in a solution of its isotope have Hevesy and Paneth gone further than has been customary in regarding a mixture of elements as one element. Such a system, however, is thermodynamically indefinite, and the line of argument deduced from the application of Nernst's formula can only be applied with caution. It is appropriate to designate the properties of isotopes, not as identical, but as equal, and there remains the important task of establishing the limits within which this equality holds. F. S.

The Question of Isotopic Elements. III. G. von Hevesy and F. Paneth (*Physikal. Zeitsch.*, 1916, **17**, 4—6).—With the admission by Fajans of the definiteness of the electrode potential measured by the authors, the only dispute as to facts vanishes. Soddy has not raised the question as to how a system will behave in which the isotopes are not mixed initially, and it was only after the authors had successfully isolated visible quantities of radium-*D* that such a case could be experimentally studied. This is an important supplementation, but no one but Fajans would be under the impression that the authors had ascribed Soddy's fundamental idea of isotopy to themselves. Words such as "our mode of representation" merely arise from the fact that Fajans had attacked, not Soddy, but the authors. The test now applied—measurement of the electrode potential between pure isotopes—enables chemical individuality to be recognised in a much more lucid manner than in the case of the precipitations of mixtures of isotopes, which are subject to suspicion, owing to adsorption processes, and the authors' results lead to the conclusion that radium-*D* and lead are actually "practically identical in chemical properties." The authors prefer their term "substitutional," rather than "identical" or "equal" in the definition of isotopes, but to pursue the problem of definition further would be to cause the controversy to assume the aspect of a mere quibble. F. S.

Electrical Resistance of Some Rare Metals; Thermo-electric Power and Rectifying Action of Germanium. Carl Benedicks (*Intern. Zeitsch. Metallographie*, 1916, **7**, 225—238).—A specimen of massive cerium, free from pores, is found to have a specific resistance of 78. Praseodymium and neodymium give the values 88 and 79 respectively. The specific resistance of ruthenium is probably about 9, the actual value found being higher on account

of porosity. Uranium has a lower resistance than bismuth, but the metal is not readily obtained free from carbide. The specific resistance of germanium lies between the values for silicon and tin.

Measurements of the thermoelectric power of germanium give as the value of the coefficient α against copper -380 ± 40 microvolts per degree. Germanium has thus, next to silicon, the highest known thermoelectric force against copper. The fact that silicon occasionally gives positive values is attributed to allotropy, as grey tin is found to be positive, whilst ordinary tin is negative.

Germanium, like silicon, exhibits a marked rectifying effect. The thermoelectric current passes much more readily in one direction than in the other, especially when the contact surface is fresh and the pressure light. This happens even when the point and plate in contact are of the same metal. The direction of the effect makes a purely thermoelectric explanation inapplicable. C. H. D.

Contact Electricity of Solid Dielectrics against Conducting and Non-conducting Liquids. ALFRED COEHN and JOSEF FRANKEN (*Ann. Physik*, 1915, [iv], **48**, 1005—1033).—A method is described by means of which it has been found possible to measure electrostatically the charge which solid dielectrics acquire when brought into contact with aqueous solutions. The contact electrical effect increases with time, but reproducible end-values are readily obtained.

Solid paraffin was employed as dielectric substance, and the influence of electrolytes and non-electrolytes on the contact effect was examined. The influence of electrolytes on the charge acquired by the dielectric is similar to that which has been previously found in experiments with gases bubbled through the aqueous solutions, but in the case of paraffin the electrolyte concentrations required for a given reduction in the magnitude of the contact effect are much greater than in the case of gases. This parallelism shows itself in the much greater influence of the hydrogen ion as compared with other ions. In all the experiments with acids, it was found possible to bring about a reversal of sign of the contact effect by increasing the concentration of the solutions. The difference in behaviour between acids and neutral salts is also shown in the temperature-coefficient of the contact effect in that temperature has little influence in the case of neutral salts and alkalis, whereas the influence of acids increases rapidly with rise of temperature. Non-electrolytes in dilute solution have no appreciable influence on the contact effect, a result which was also obtained in experiments with gases. H. M. D.

The Electrical Resistance of Acetic Acid in the Solid and Liquid Phases. J. H. L. JOHNSTONE (*Trans. Nova Scotian Inst. Sci.*, 1912–1913, **13**, 191—208).—The influence of temperature on the electrical resistance of acetic acid has been examined over the range $-80°$ to $27°$, and the influence of small quantities of water on the resistance determined.

The acetic acid was prepared by fractional freezing of a sample

which contained 99·55% of acetic acid, but it is not claimed that water was completely eliminated by this treatment. The presence of water is indicated by the fact that a sharp change in the resistance was observed at the eutectic temperature ($-26·55°$) as well as at the melting point of the acid. For a particular sample of acid the resistance changed suddenly from 10^{10} below to $8·8 \times 10^8$ above the eutectic temperature, and from $1·27 \times 10^9$ below to $3·52 \times 10^7$ above the m. p. The variation of the resistance in the interval between the eutectic temperature and the m. p. is anomalous, but can be explained in terms of the changing concentration of the liquid phase which is present. The conductivity of the acid in this region is due almost entirely to the presence of traces of water.

H. M. D.

Galvanic "Exaltation" of Metals by Alcohol. CH. M. VAN DEVENTER (*Chem. Weekblad*, 1916, **13**, 173—183).—A further contribution to the author's theory of the leaking insulator. A. J. W.

New Thermoelectric Method for the Study of Allotropy of Iron or Other Metals. C. BENEDICKS (*Compt. rend.*, 1916, **162**, 297—299. Compare *J. Iron Steel Inst.*, 1914, **1**, 434).—The metal was examined in the form of a fine wire, which was drawn at a constant velocity of 1·6 mm. per second through a small electric furnace maintained at a constant temperature, measured by a Le Chatelier couple. Measurements were made of the *E.M.F.* developed at different temperatures. The curve for the sample of iron examined, which was remarkably pure, showed a marked discontinuity corresponding with the point A_3, but for the point A_2 no discontinuity was found. The curves obtained for this effect resemble the dilatation curves. W. G.

Magneto-chemical Effect. A. N. SCHTSCHUKAREV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1644—1668).—The author assumes that the process of chemical combination or, in general, of the mutual action between two impinging molecules is equivalent to an electric discharge, so that the medium in which such chemical process takes place will represent a collection of such discharges proceeding in all possible directions. In a magnetic field there should be an increase in the number of discharges perpendicular to the lines of the field and, therefore, a temporary difference of potential in the same direction. In a vessel situate in a magnetic field were arranged, parallel to the lines of the field, two similar pieces of platinum foil perfectly identical as regards electromotive force. When these plates were connected through a galvanometer and the vessel was charged with ferric chloride solution, no deflection was observed, but addition of potassium iodide to the liquid caused an immediate deflection. This phenomenon of chemical polarisation accompanies many other, and possibly all, reactions. As a rule, the smaller of the platinum plates becomes negatively, and the larger positively, electrified. With one and the same pair of platinum plates, the deflection gradually diminishes, owing to their exhaustion, but the latter effect may be reduced by occasional immersion

of the plates in concentrated hydrochloric acid. Thus, the initial magnitude of the current of chemical polarisation varies, but in every case the current exhibits a very gradual diminution, which probably extends over the whole time occupied by the reaction.

The existence of the current of magnetic polarisation referred to above has been actually observed (1) with reactions proceeding freely, and (2) with reactions taking place at electrodes during electrolysis. The results obtained appear to indicate a connection between this magnetic effect and diminution in valency. The magnetic effect is, indeed, observed only with reactions in which there takes place a lowering of the valency of one of the reacting ions, such as occurs in the reactions between ferric chloride and potassium iodide, chromium trioxide and hydriodic acid, and vanadium tetrachloride and potassium iodide. If, however, the liberation of iodine takes place, not on account of the depression of the valency of one of the reacting ions, but on account of the decomposition of a complex ion or a non-ionised complex, or if the diminished valency of one of the reacting ions is compensated by increased valency of another, as in the reaction $2FeCl_3 + SnCl_2$, no magnetic effect is observed.

Examination of a number of cases in which the magnetic effect accompanies electrodic changes leads to the following conclusions: Complex ions which, on separation, react only with water, such as OH, NO_3, SO_3, $CH_3{\cdot}CO_2$, CN, S_2O_8, ClO_4, give no magnetic effect, but when ions, for instance, SO_4, separating from an -ous salt, unite immediately with the dissolved salt forming an -ic salt, a marked magnetic effect is observed. $Zn^{\cdot\cdot}$ and $Fe^{\cdot\cdot}$ give no magnetic effect, but $Fe^{\cdot\cdot\cdot}$ gives a very strong effect, which changes its sign. With rare exceptions, the sign of the magnetic effect is constant for a given reaction or for the separation of a given ion. It appears strange that $Ca^{\cdot\cdot}$ gives no effect, whereas with $Mg^{\cdot\cdot}$ the effect is very marked. Particularly intense magnetic effects are given by reactions accompanied by separation of ions of the halogens; with bromine and iodine an almost constant negative effect is observed with a normal field, and this is also the case with the separation of chlorine ions from a whole series of salts, although with another series of chlorides a marked positive effect is observed. No effect is produced in cases where the liberated chlorine undergoes immediate combination; this is the case, for instance, with the reaction $SnCl_2 + Cl_2 = SnCl_4$, or when a small proportion of allyl alcohol is added to a solution of barium chloride. T. H. P.

Thermal Expansion and Compressibility of Liquids at Low Temperatures. W. SEITZ, H. ALTERTHUM, and G. LECHNER (*Ann. Physik*, 1916, [iv], **49**, 85—92).—In the expectation that the properties of liquids would show a tendency to approximate at low temperatures to those characteristic of solids, measurements have been made of the change of the specific volume of a number of liquids of low freezing point. For *iso*pentane and ethyl ether the coefficient of thermal expansion diminishes with falling temperature down to $-120°$, the lowest temperature at which observations were

made. For methyl alcohol and ethyl alcohol the coefficient decreases at first, attains a minimum at about $-40°$, and at lower temperatures increases. Carbon disulphide was found to behave similarly, the minimum in this case corresponding with a temperature between $-70°$ and $-80°$. H. M. D.

Thermal Expansion and Compressibility of Liquids at Low Temperatures. W. SEITZ and G. LECHNER (*Ann. Physik.*, 1916, [iv], **49**, 93—115. Compare preceding abstract).—The compressibility of *iso*pentane, ethyl ether, methyl alcohol, ethyl alcohol, and carbon disulphide has been determined at temperatures between 0° and $-110°$ and at pressures up to 1000 atmospheres. As the pressure increases, the tendency of the coefficient of expansion to increase with falling temperature becomes much more marked than at atmospheric pressure. H. M. D.

[Determination of the Velocity of Sound in Gases.] C. DIETERICI (*Ann. Physik*, 1915, [iv], **48**, 1122—1124).—A reply to Schweikert's criticism (this vol., ii, 79) of the results obtained in previous measurements of the velocity of sound in gases. The results in question are shown to be in good agreement with Schweikert's own data. H. M. D.

A Criticism of van der Waals's Equation and Some New Equations Derived Therefrom. JAMES KAM (*Phil. Mag.*, 1916, [vi], **31**, 22—36).—From a consideration of the influence of a and b on the pressure-volume relations the author arrives at the formula $P+a/(V+b)^2=RT/V$ as an alternative to the van der Waals's equation. According to this formula, an actual gas of density $1/(V+b)$ exerts the same pressure as an ideal gas of density $1/V$. The analysis of the formula leads to the conclusion that the density in the critical condition is for all substances two-thirds of the density of an ideal gas which at the same volume exerts a pressure equal to the critical pressure at the critical temperature.

If the internal pressure is denoted by P_1 so that the total pressure $\pi=P+P_1$, then it is shown that the critical values of P and P_1 are equal, or $P_c=P_{1c}$, and further that $P_c=RT_c/2V_c$ and $\pi_c=RT_c/V_c$, according to which the ideal gas law is applicable to the critical condition. Experimental data in support of the validity of this relation are cited.

The equality of P_c and P_{1c} is supposed to be connected with the disappearance of the surface tension and of the latent heat of vaporisation at the critical point. When this equality obtains the cohesive forces are exactly counterbalanced by the thermic pressure, and the transference of a molecule from the interior of the liquid to the space above it requires no expenditure of energy. H. M. D.

The Variation of Surface Tension with Temperature. ALLAN FERGUSON (*Phil. Mag.*, 1916, [vi], **31**, 37—47).—It is shown that the variation of the surface tension of liquids with temperature

can be represented by the equation $T=T_0(1-b\theta)^n$, in which T is the surface tension at temperature θ, T_0 the tension at 0°, and b and n are constants characteristic of the substance. Since $T=0$ at the critical temperature θ_c, it follows that $\theta_c=1/b$. The critical temperatures calculated in this way are found to be in close agreement with the observed values for some fourteen non-associated liquids which have been examined. The value of b varies from 0·002793 for chlorobenzene to 0·005155 for ethyl ether, but n varies very little from the mean value of 1·210. This mean value may be employed generally without seriously detracting from the accuracy of the formula.

In the group of esters $R\cdot CO_2R_1$, the value of b diminishes with increase of R or R_1, and is greater for an *iso*-compound than for the corresponding normal ester. Moreover, R and R_1 cannot be interchanged without alteration in b, and this has the greater value when the more complex radicle is associated with the carbonyl group. In esters of the series $R\cdot CO_2Me$, the value of b is apparently connected with the boiling point, θ, of the ester as expressed by the equation $b=c/(d-n)\theta-273c$, in which c and d are constants and n is the number of carbon atoms in R.

The empirical relations connecting the temperature-coefficient of the surface tension of a liquid with its critical temperature, which have been pointed out by Walden (A., 1909, ii, 122), are discussed in relation to the author's formula. H. M. D.

Thermodynamics and Fractional Distillation. E. CHENARD (*Bull. Assoc. chim. Sucr. Dist.*, 1916, **33**, 47—55).—A discussion of the influence of various factors on the separation of the components of binary liquid mixtures by fractional distillation, with special reference to mixtures of ethyl alcohol and water. It is pointed out that the rate of flow of the vapour and the difference in density of the components exert an influence on the fractionation which is of practical importance, and may lead to results which are quite different from those anticipated from a consideration of the thermodynamic equilibrium between the liquid and vapour phases.

For the construction of improved forms of distillation apparatus it is shown that the design must be such as to permit of free passage of the vapour and rapid removal of the condensed liquid. The fractionating column should be disposed horizontally or nearly so, and the number of fractionating elements should be considerable.

Actual experiments with apparatus constructed on these lines have shown that much better results can be obtained than by the use of apparatus of the usual type. H. M. D.

Heats of Formation of Additive Organic Compounds. IV. Picrates. B. L. VANZETTI and V. GAZZABIN (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 527—532; *Gazzetta*, 1916, **46**, i, 145—151. Compare A., 1913, ii, 296).—The heats of formation of the picrates of certain bases of the pyridine group, now given, indicate clearly the differences existing between compounds of picric acid with tertiary amines, such as pyridine and quinoline, and those of the same acid

with the corresponding hydrogenated, secondary bases, in which the nitrogen-containing group has lost completely the aromatic character. The following are the mean molecular heats obtained, in large calories: pyridine picrate (m. p. 164°), 13·84; piperidine picrate (m. p. 151—152°), 20·56; quinoline picrate (m. p. 204°), 13·2; tetrahydroquinoline picrate (m. p. 141·5°), 9·9. T. H. P.

Physico-chemical Force of Attraction. II. N. A. KOLOSOVSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2035—2037).—Reply to Gurvitsch (A., 1915, ii, 747). T. H. P.

The Law of Solubility. HENRY LE CHATELIER (*Compt. rend.*, 1916, **162**, 245—246).—A reply to Colson (compare this vol., ii, 129). W. G.

Ultramicroscopy of Crystallisation Phenomena. I. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2140—2163).—After discussing the capacity of highly disperse particles for vectorial growth, etc., experiments are described on the formation and disaggregation with the disperse particles of skeletons of sodium chloride in silicic acid gels. From the results obtained under different experimental conditions and the microscopic and ultramicroscopic appearance of the crystalline systems obtained, a number of general conclusions are drawn. Crystalline skeletons and dendritic growths, resulting from the prevention of regular crystalline development by marked initial supersaturation or obtained in a disperse medium, may be regarded as coalitions of disperse particles, which are to some extent irregularly orientated to one another. These crystalline systems, in consequence of the great development of their external and internal surfaces, the latter the result of rupture of the crystalline homogeneity, exhibit instability and break down into disperse particles of a different degree of dispersion; this disaggregation is accelerated by small oscillations of the temperature. The disperse systems thus formed undergo gradual diminution of their dispersion, and the disperse particles then tend to consume one another and thus yield crystals with complete outlines. The capacity for vectorial growth shown by large crystals is inherent in particles of all degrees of dispersion, including those at the extreme limit of ultramicroscopic vision. Precipitates formed by the disaggregation of dendritic systems and consisting of particles which do not reveal their crystalline form when examined ultramicroscopically, are still undoubtedly crystalline. When dissolved, these crystalline formations, characterised by marked development of their external and internal surfaces or by rupture of the crystalline homogeneity, undergo disruption into disperse particles, this process preceding solution. T. H. P.

Materials for Experimental Dispersoidology. I. Preparation of any Substance in any Degree of Dispersion. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2133—2139).—The author discusses the colloidal condition as a general property of

matter (compare A., 1910, ii, 940), and describes again the experiments with sodium chloride (A., 1913, ii, 31). Further results are given in succeeding papers. T. H. P.

Materials for Experimental Dispersoidology. II. Gels and the Process of Gelatinisation. P. P. von Weimarn (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2163—2176).—When a gel is formed by the more or less uniform gelatinisation of a liquid throughout its entire mass the author terms it reticulated, and when the gelatinisation takes place at definite surfaces within the liquid, coarsely-cellular. A gel of the latter type is obtained, for instance, when saturated aqueous barium thiocyanate is added to saturated manganous sulphate solution, every drop or stream of the added liquid becoming coated with a transparent membrane of gel. Systems analogous to coarsely-cellular gels are obtainable with ice by pouring drops of water into alcohol cooled in a mixture of carbon dioxide and ether or in liquid air; it is difficult to fix the gelatinous form of the ice membranes for any length of time, but the structure of these membranes may be examined microscopically and ultramicroscopically, and is found to be identical with that of gelatinous membranes of barium sulphate. The formation of membranes in this case is due to the fact that at such low temperatures the water is able to diffuse scarcely at all into the alcohol, and is almost instantaneously solidified in a highly disperse state. Reticulated gels of ice are obtainable particularly easily near the eutectic point of the water–alcohol system. Membranes of coarsely-cellular gels are closely comparable with sections of corresponding thickness of reticulated gels cut by means of a microtome. Many observations confirm the view that the process of gelatinisation and the formation of distinctly microcrystalline precipitates are essentially identical, and differ only in degree.

The swelling, spontaneous dispersoid solution, and gelatinisation of sodium oleate in toluene, xylene, and benzene have been investigated, the observations made being in complete agreement with those of the same processes with barium sulphate, gelatin, aluminium hydroxide, etc., confirming the conclusion that a gel is a sponge composed of highly disperse, crystalline granules soaked in dispersive medium. T. H. P.

Materials for Experimental Dispersoidology. IV. Disperse Systems of Cupric Chloride in Benzene. P. P. von Weimarn and I. B. Kagan (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2215—2251).—The conditions of formation and certain properties of the following disperse systems have been investigated: With the liquid disperse phase, $x\mathrm{H_2O}+y\mathrm{HCl}$; with the solid disperse phase, $\mathrm{CuCl_2}$; with the solid disperse phase, $x\mathrm{CuCl_2}+y\mathrm{CuCl_2,2H_2O}$; with the solid disperse phase, $\mathrm{CuCl_2,2H_2O}$, this being the first example found of a typical crystallo-hydrate in the disperse state; with the solid disperse phase, $\mathrm{CuCl_2,2H_2O}$, and the complex liquid disperse phase $(x\mathrm{H_2O}+y\mathrm{HCl}+z\mathrm{CuCl_2})$ and $(x\mathrm{H_2O}+y\mathrm{HCl})$; with the solid disperse phase, $(x\mathrm{CuCl_2}+y$ copper oleate); with the solid disperse

phase, ($x CuCl_2,2H_2O + y$ copper oleate). Confirmation is obtained of the theory according to which, in a medium either almost completely passive or very active, the stability of dispersoid solutions is small. The colour of dispersoid solutions is nearly identical with that of true solutions and that of coarse disperse phases, but is less intense than the latter, and, with a sufficiently high degree of dispersion, is turbid; it is hence possible to judge by the colour of the course of chemical and physical transformations of disperse phases. T. H. P.

Nature of the Elastic and Plastic Conditions of Matter. I. I. OSTROMISSLENSKI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1995—2014).—The two new constants for colloids, namely, the elasticity point and the fatal temperature (this vol., i, 54, 55), permit of the characterisation of two new states of aggregation of matter: (1) the plastic state, in which a substance exists in the interval of temperature between the elasticity and fatal points, and (2) the elastic state, corresponding with the interval between the elasticity point and the melting point. The supposition that these states of aggregation are properties of all colloids is confirmed experimentally, and since the colloidal condition is common to all forms of matter, the elastic and plastic states are general forms of aggregation. The normal course of the changes in the condition of aggregation is expressed by the scheme: solid $\rightleftarrows$ plastic $\rightleftarrows$ elastic $\rightleftarrows$ liquid $\rightleftarrows$ gas. Many substances follow exactly this scheme of transformations before reaching the temperatures at which their molecules undergo decomposition, but others melt with previous conversion into only one of these intermediate states or into neither of them. Such substances correspond with the following incomplete schemes: solid $\rightleftarrows$ plastic $\rightleftarrows$ liquid, solid $\rightleftarrows$ elastic $\rightleftarrows$ liquid, or solid $\rightleftarrows$ liquid, and cannot be obtained in the plastic or elastic condition by simple change of temperature.

The methods available for obtaining matter in the plastic or the elastic state are as follows: (1) By change of temperature. Various individual compounds and mixtures, such as caoutchouc and some of its homologues, polymeric acrylic esters, factis, gels of gelatin, etc., exist in the elastic condition at the ordinary temperature, and others, such as guttapercha, camphor, copper oleate, paraffin wax, ozokerite, etc., in the plastic state. The transformation from the elastic to the plastic state is always realisable, since it accompanies lowering of temperature, but that from the plastic to the elastic condition, by rise of temperature, does not always occur, since fusion or decomposition may take place before the elasticity point is reached. In such cases one of the two following methods must be employed. (2) By introduction of a foreign liquid. This liquid must be able to act as a medium in which the given colloid either dissolves or swells, the process of solution being intimately connected with the plastic condition of matter and that of swelling with the elastic state. Solids which neither dissolve nor swell in liquid media cannot be obtained in either the elastic or plastic state by this method. For example, caouprene chloride readily swells in

carbon disulphide at the ordinary temperature, giving an elastic substance possessing all the properties of natural caoutchouc, but exhibiting instability owing to the ease with which the carbon disulphide is lost. Again, the compound of isoprene with sulphur dioxide, $(SO_2)_m n(C_5H_8)_8$, is a typical solid, with a fatal temperature above the ordinary temperature; when heated, it is converted first into the plastic condition and then approximately into the elastic form, but at this point decomposition begins. If, however, this compound is precipitated by alcohol from its solution in hot aniline, it yields the complex $n(C_5H_8)_8,(SO_2)_m + pNH_2Ph + q$Et·OH, which at the ordinary temperature exhibits, qualitatively and quantitatively, the association of elastic properties of ordinary caoutchouc, its elasticity point being below 0°. (3) By supercooling liquid masses. By rapid and intense supercooling, for instance, to $-100°$, a liquid or fused solid may be obtained in an elastic or plastic modification at a temperature corresponding normally with the solid form alone. This method is generally known, and is used principally for obtaining substances in amorphous, solid, vitreous modifications; the plastic and elastic states represent intermediate stages. Thus, by rapid and profound cooling, water is obtained first in the elastic, then in the plastic, and finally in the vitreous modification, and similar behaviour is shown by almost all liquids.

Substances in the plastic or elastic condition are not to be regarded as mere mechanical mixtures of a solid and a liquid, although their peculiar properties are due to mutual action of a solid and liquid. When a liquid or fused substance is rapidly and intensely cooled, the low temperature causes reduction in the velocity with which its solid phase appears, so that part of the substance retains its liquid consistency; into this portion the nascent solidified part swells, the elastic or plastic modification being thus obtained at temperatures corresponding normally with the solid phase. The following principles are deduced: (1) The transformation of a solid into a liquid usually commences considerably below its melting point. (2) Every given temperature of a substance corresponds with a definite, stable equilibrium between its solid and liquid phases. With this equilibrium there corresponds, with any substance, a definite association of elastic or plastic properties; in particular, for a certain temperature interval the proportion of one of the phases may be zero.

A colloidal solution of a solid substance containing the latter partly in the solid state should, when heated, behave in a definite manner, independently of the nature of the solvent. Since, also, with every temperature there corresponds a definite equilibrium between the solid and liquid phases, the solid will be converted successively into the plastic, elastic, and liquid states, independently of the condition of aggregation of the surrounding medium; this process should, therefore, take place both in a gaseous medium and in colloidal solution. It has been already found that the elasticity point and the fatal temperature may be determined by means of either the substance in the free state or its colloidal solution. The melting points of colloidal substances are also measurable in an

analogous manner, that is, by the change in direction of the curves expressing the dependence of physical properties on the temperature (this vol., i, 55). The temperature thus determined would correspond with the disappearance of the solid phase in the given colloidal solution, and in reality it may be accompanied by either (1) separation of the solution into two layers, or (2) its conversion into a molecular disperse solution, or (3) the formation of a colloidal solution of a liquid in the same solvent. T. H. P.

Non-, Uni-, and Bi-variant Equilibria. IV. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1018—1025. Compare this vol., ii, 19).—A further consideration of types of equilibrium in heterogeneous systems, with special reference to the general case of a system of n components. The $n+2$ equations, which are required to define the univariant equilibria, are not independent of one another. Two of these equations only are required for the determination of the remainder. H. M. D.

Non-, Uni-, and Bi-variant Equilibria. V. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1026—1037. Compare preceding abstract).—It is shown that the different types of pressure-temperature diagram corresponding with any system of n components may be deduced without a knowledge of the concentration diagram or the composition of the phases. H. M. D.

Determinations in the System Lead Sulphate, Sulphuric Acid, and Water. A. D. DONK (*Chem. Weekblad.*, 1916, **13**, 92—97).—An application of Schreinemakers's graphic method to mixtures of lead sulphate and dilute sulphuric acid. A. J. W.

Swelling of Hides in Presence of Hydrogen Ions. G. POVARNIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2064—2073).—The work of other investigators, notably Paessler and Appelius (*Gerber-Zeit.*, 1902, **45**), in this direction is discussed. The velocity with which hide-material swells in pure water is expressed by the equation $\log[M/(M-Q)] = 0{\cdot}4343k_1t$ (1), and the swelling in presence of acid depends on the following considerations: (*a*) The velocity of swelling is directly proportional to the velocity of the acid ions in penetrating the membrane (hide), and this velocity is proportional to $\sqrt{t}$, as was shown by Morse and Pierce (A., 1904, ii, 14) for gelatin; in absence of acid, the swelling is proportional to the velocity with which the ions of water pass through the membrane, that is, to t. (*b*) The rate of swelling is inversely proportional to the quantity of the hide-material dissolving at the surface of contact of hide and liquid, and, since this swelling is directly proportional to the time, the rate of swelling is inversely proportional to t. (*c*) The maximum swelling, M, for a given acid is equal to some constant maximum, M_0, multiplied by k_0, which is a coefficient varying with the nature of the acid; it may be assumed that k_1 of equation (1) is in general equal to some magnitude, $k/2$. (*d*) The

rate of swelling is proportional to the index of basicity, n, of the acid, if the latter is completely dissociated, and in general it should be proportional to the number of free hydrogen ions in the solution of the given acid. On these theoretical foundations the equation $\log[M/(M-Q)]=0{\cdot}4343nk\sqrt{t}$ is constructed. It is found that Paessler and Appelius's results for five acids at concentrations of 0·1—0·6% are expressed satisfactorily by this equation, $0{\cdot}4343k$ having the value 0·274, whilst n is equal to 1 or, with strongly dissociated dibasic acids, 2; M is a variable magnitude depending on the character and concentration of the acid. T. H. P.

Interaction of Benzoyl Chloride and *m*-Xylene in Presence of Haloids of Various Metals of the Second Group. B. N. Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1853—1884).—By absorption of the hydrogen chloride liberated in potassium hydroxide solution, the author has measured the velocity of the reaction $Ph{\cdot}COCl + m\text{-}C_6H_4Me_2 = C_6H_3Me_2Bz + HCl$ at 158° in presence of varying proportions of haloids of metals of group II. The following considerations have a bearing on the results obtained. When antimony trichloride or tribromide is present (compare A., 1914, i, 188, 673), this forms a molecular compound with the aromatic hydrocarbon readily soluble in the latter, so that the reaction with the chloroanhydride proceeds in a perfectly homogeneous medium. The halogen salts now investigated, with the possible exception of those of zinc and mercury, are quite insoluble in either benzoyl chloride or *m*-xylene or in mixtures of the two, and, as far as can be seen, enter into reaction with neither of the reacting compounds; in these cases, then, the media are heterogeneous. Further, although most of the salts are kept thoroughly mixed with the liquid by a current of air passing through the latter, this is not the case with such heavy salts as mercuric chloride and bromide; in these instances, then, the values of the velocity constants obtained are lower than the true values.

The values of the velocity constant obtained when approximately 0·5 or 1·0 mol. of the haloid is taken per 1 mol. of each of the reacting compounds are as follows, the first figure in each case giving the absolute value, followed by the relative value in brackets: $1CaCl_2$, K_2 $0{\cdot}0^{5}15$ (1); $0{\cdot}94CaBr_2$, K_2 $0{\cdot}0^{5}14$ (1); $0{\cdot}98SrCl_2$, K_2 $0{\cdot}0^{5}63$ (5); $0{\cdot}5SrBr_2$, K_2 $0{\cdot}0^{4}23$ (16); $0{\cdot}48BaCl_2$, K_2 $0{\cdot}0^{5}78$ (6); $0{\cdot}5BaBr_2$, K_2 $0{\cdot}0^{4}13$ (9); $0{\cdot}57CdCl_2$, K_2 $0{\cdot}0^{4}62$ (44); $0{\cdot}51CdBr_2$, K_2 $0{\cdot}0^{4}17$ (12); $0{\cdot}49MgCl_2$, K_2 $0{\cdot}0^{4}15$ (11); $0{\cdot}51HgCl_2$, K_2 $0{\cdot}0^{3}34$ (243); $1{\cdot}03HgBr_2$, K_2 $0{\cdot}0^{2}45$ (3214); $0{\cdot}53ZnCl_2$, K_2 0·0110 (7857); $0{\cdot}52ZnBr_2$, K_2 0·0121 (8643). In presence of the zinc and mercuric salts, the velocity constant increases only to a maximum value, given above, these maxima being obtained with $0{\cdot}38ZnCl_2$, $0{\cdot}26ZnBr_2$, $0{\cdot}18HgCl_2$, and $0{\cdot}26HgBr_2$ respectively. The values of K_2 corresponding with the presence of 1·03, 0·53, 0·5, 0·38, 0·27, 0·105, and $0{\cdot}013ZnCl_2$ are 0·0125, 0·0110, 0·0106, 0·0112, 0·0071, 0·0047, and 0·00021. The variation of K_2 with the concentration of the halogen salt is here quite different from that found when varying proportions of antimony trichloride are present, since K_2 is then almost exactly

proportional to the square of the concentration of the trichloride (*loc. cit.*). The use of zinc chloride and bromide in organic syntheses is now under investigation. T. H. P.

Velocity of Decomposition of Electrolytes in the Light in Relation to their Degree of Electrolytic Dissociation. C. BONGIOVANNI (*Gazzetta*, 1916, **46**, i, 127—135).—The fact that the instability of perchloric and nitric acids is not shown by aqueous solutions of these acids or by the corresponding salts, Ostwald ("Principles of Inorganic Chemistry") regards as due to the occurrence in the latter cases of the stable perchloric or nitric ion, which is not present in the anhydrous acids. The author considers this conclusion unfounded, and points out that water often has a positive or negative catalysing influence on the decomposition of compounds dissolved in it, and further that the latter often combine with the water, yielding compounds differing in stability from the anhydrous compounds. A number of cases are quoted in support of this view. The results of the author's own experiments are as follows.

The velocity of decomposition of oxalic acid in dilute aqueous solution by the action of sunlight is considerably diminished by the presence of sulphuric acid, and the depression of the freezing point of the solution containing the two acids is far less than the sum of the depressions observed with solutions of the two acids taken separately. According to Ostwald's hypothesis, similar behaviour should be shown by solutions of oxalic acid and potassium oxalate. In this case, however, the presence of potassium oxalate causes marked retrogression of the degree of dissociation of oxalic acid, but this is not accompanied by any variation in the stability of the acid towards sunlight. These results appear to exclude the assumption that the molecule of oxalic acid exhibits a stability towards light different from that of its ion. T. H. P.

A Kinetic View of Catalysis. H. J. PRINS (*Chem. Weekblad.*, 1916, **13**, 127—131).—A theoretical paper. A. J. W.

The Influence of Different Surfaces on the Decomposition of Methane. WILFRID ERNEST SLATER (T., 1916, **109**, 160—164).—The influence of different surfaces on the thermal decomposition of methane has been investigated in comparative experiments at 910°, in which the gas was exposed to equal surfaces of different substances for equal intervals of time, and the decomposition measured by the amount of hydrogen in the residual gas. The various substances examined were used in the form of fine powders which had been sifted through fine gauze, and were disposed in two porcelain boats placed end to end along the middle portion of the electrically heated porcelain tube.

The results obtained with silica, alumina, magnesium oxide, calcium oxide, barium oxide, wood charcoal, graphite, carborundum, iron, and copper show that the rate of decomposition of methane

depends not only on the extent of the hot surface which is exposed to the gas, but also on the nature of the substance concerned.

H. M. D.

Velocity of Hydrogenation of Fumaric Acid with Colloidal Palladium as Catalyst. A. KOREVAAR (*Chem. Weekblad.*, 1916, **13**, 98—107).—The author points out that the velocity of hydrogenation of fumaric acid with colloidal palladium as catalyst is dependent on the rapidity of revolution of the stirring apparatus, and describes a form of stirring gear with which the velocity of revolution can be measured and controlled. A. J. W.

The Metastability of the Elements and Chemical Compounds in Consequence of Enantiotropy or Monotropy, and its Bearing on Chemistry, Physics, and Technics. I. ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 961—965). —Observations on the enantiotropic yellow and red modifications of thallous picrate are described, which show that the dry substances may be heated or cooled far above or below the transition temperature without change. If traces of a solvent such as water, ethyl alcohol, methyl alcohol, or ether are added, the retardation phenomena are not observed.

It is suggested that arrested transformation may be of frequent occurrence amongst the non-metals and chemical compounds, and that this property is not confined to the metals. H. M. D.

Integral Atomic Weights. I. and II. FRANK WILLIAM DODD (*Trans. Nova Scotia Inst. Sci.*, 1912–1913, **13**, 216—221, 223—227). —I. It is suggested that the properties of the elements are functions of integral atomic numbers which are greater than the accepted atomic weights to an extent depending on the density of the element in accordance with the relation $I.N - A.W = 1{\cdot}8D$, where I . N is the integral atomic number, A . W the atomic weight, and D the density. Such properties are the specific heat and the m. p.

II. To meet the criticism that the relation between integral atomic number, atomic weight, and density will depend on the temperature at which the density is measured, it is suggested that each element has a natural density, any departure from which is more or less accidental. H. M. D.

Prout in Connexion with Avogadro's Hypothesis. LEONARD DOBBIN (*Chem. News*, 1916, **113**, 85).—Avogadro's hypothesis (1811) which was not generally accepted until some years after the publication of Cannizzaro's "Sunto di un corso di filosofia chimica" in 1858, was clearly stated by Prout in his "Chemistry, Meteorology, and the Function of Digestion considered with reference to Natural Theology," which was published in 1834. Prout's views, which were adopted without knowledge of the essays of Avogadro, Ampère, and Dumas, were criticised by W. C. Henry (*Phil. Mag.*, 1834, [iii], **5**, 33), but were not otherwise noticed until 1904 (see A. N. Meldrum, "Avogadro and Dalton"). N. H. J. M.

Valency of the Elements. III. G. POVARNIN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1737—1769. Compare A., 1915, ii, 761).—The author develops further his theory of polar affinities and discusses the views of Tschitschibabin, who states ("Investigations on Tervalent Carbon"): "Valency is a number denoting how many atoms are in immediate union with the given atom." "Valency, and also the degree of saturation, that is, the store of chemical energy of an individual atom, is a function of the atoms and groups entering into combination with such atom." "The strength of the separate valency of each atom is not a constant magnitude, but varies . . . in dependence on the remaining radicles united with the atom." The insufficiency of these views is maintained, particularly with reference to various points connected with derivatives of "tervalent" carbon, and it is claimed that the author's hypothesis gives more reasonable explanations of such points. T. H. P.

Steam Apparatus with Constant Water Supply. J. TRAMBICS (*Chem. Zeit.*, 1916, **40**, 128—129).—A simple apparatus consisting of a boiler of thin metal provided with a constant level tube similar to that used for water-baths, except that it is attached to the water-tap, and has two tubes connecting it with the boiler, one below and the other above the water level; the outlet is connected with a **U**-tube, which gives a pressure in the apparatus corresponding with the column of water. A mercury regulator is employed for the gas supply.

A sketch of the apparatus is given. N. H. J. M.

Inorganic Chemistry.

Bromine Ion Content of Sea-water. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1916, **29**, 68. Compare this vol., ii, 109).—Water from the Adriatic was found to contain 63·81 mg. of bromine per litre; the chlorine amounted to 18375 mg. per litre. W. P. S.

Catalytic Method for the Separation of Solid Iodine from Solutions. L. PISARSHEVSKI and N. AVERKIEV (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2057—2060).—The action of chloric acid on iodine ions in an acid solution, resulting in the deposition of iodine, thus, $6H^{\cdot} + 6I' + ClO_3' = 3H_2O + Cl' + 3I_2$, is greatly accelerated by the presence of ferri-ions in small concentration, which act as a catalyst; the iodine is precipitated as a fine powder or as more or less large, well-formed crystals, according to the concentration of the iodine solution, the amount of catalyst added, the composition of the liquid, and certain other factors. The ferri-ions are converted into ferro-ions according to the equation $Fe^{\cdots} + I' = Fe^{\cdot\cdot} + I$, the

ferro-ions being then oxidised thus: $6Fe^{\cdot\cdot} + 6H^{\cdot} + ClO_3' = 3H_2O + Cl' + 6Fe^{\cdot\cdot\cdot}$. The method is applicable to the separation of iodine, not merely from solutions of pure iodides, but from the brine obtained on leaching with water the ashes of seaweed, and is carried out as follows: To the iodide solution, acidified with excess of sulphuric or hydrochloric acid, are added (1) potassium chlorate in the proportion indicated by the above equation or a greater proportion if other substances capable of oxidation are present, and (2) a small volume of a solution of a ferric or ferrous salt in three times its weight of water. T. H. P.

Electrolytic Method of Obtaining Solid Iodine from Solution. L. PISARSHEVSKI and S. TJELNI (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2060—2063).—The authors describe preliminary attempts to devise a method of separating iodine electrolytically from solutions containing iodides, bromides, and chlorides (compare Specketer, A., 1899, ii, 123). Lead electrodes, or a lead anode and a carbon cathode, give good results; the lead anode becomes coated with a thin layer of lead iodide, which prevents further combination with the iodine, the latter being deposited in a crystalline crust easy to remove. T. H. P.

Materials for Experimental Dispersoidology. III. Coloured Solutions of Sulphur. P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2177—2214).—The author gives first a summary of the literature dealing with coloured solutions of sulphur, and then his own investigations, which lead to the following results: Sulphur dissolves with an indigo or blue coloration in water, ethyl, propyl, *iso*butyl and amyl alcohols, acetone, glycerol, and ethylene glycol if these solvents are rendered alkaline; with the last two solvents it is, indeed, unnecessary to add alkali, but this may come from the glass. When the above solvents are neutral or acidified, no blue colour appears. Any solution of a polysulphide becomes blue when heated if the solvent is not acid in character, and does not decompose sulphides in general, and by variation of the concentration and temperature such solutions may be obtained of any colour in the spectrum. The blue colour observed in the above cases and that exhibited by fused potassium chloride and sulphur, solutions of sulphur in ammonia or sulphur trioxide, etc., occurs when the linking of the sulphur in these compounds, which are classed together as "sulphydrates," is weakened, that is, when the sulphur atoms approach a condition of freedom from combination. The blue colour may appear over an interval of temperature ranging from $-80°$ to $+800°$. T. H. P.

Black Phosphorus. I. A. SMITS, G. MEYER, and R. PH. BECK (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 992—1007).—The black phosphorus obtained by Bridgman (A., 1914, ii, 647) has a much greater density (2·69) than that found for violet phosphorus (2·21—2·34), and this would seem to support the view that it represents a new modification.

Attempts to compare the vapour pressures of black and violet phosphorus gave unsatisfactory results on account of the difficulty of removing from the former the kerosene which had been used as pressure-liquid in its preparation. At temperatures below 550° the vapour pressure of black phosphorus did not reach a constant value. At somewhat higher temperatures, a constant value was reached, and this was very nearly equal to the vapour pressure of violet phosphorus. At 570° the black modification has a higher vapour pressure than the violet form. In presence of iodine as catalyst, the melting points of the black and violet forms were found to be 587·5° and 589·5° respectively.

The relation between the two modifications is discussed with especial reference to the fact that it has not yet been found possible to convert violet into black phosphorus even under pressures up to 12,500 kilograms per cm.^{2}. H. M. D.

Molecular Volumes of the Hyponitrites of the Alkali Metals and Metals of the Alkaline Earths. PRAFULLA CHANDRA RÂY and RAJENDRALAL DE (T., 1916, **109**, 122—131).—The densities of the solid substances were determined by means of a pyknometer with xylene as filling liquid. The molecular volumes of the anhydrous sodium, silver, and mercurous salts are 42·98, 47·96, and 62·76 respectively, and of the calcium, strontium, and barium salts, 39·61, 55·05, and 50·75 respectively. The molecular volume of the strontium salt is evidently anomalous in that it is much larger than that of the barium salt. This anomaly is not met with when the volumes of the nitrites and nitrates are compared. It may be connected with the fact that strontium hyponitrite loses its water of crystallisation much more readily than the calcium and barium salts. The latter two crystallise with $4H_2O$, but the strontium salt crystallises with $5H_2O$. The molecular volumes of the crystalline hydrates were also measured, giving 93·83, 109·3, and 98·26 for the calcium, strontium, and barium salts respectively. H. M. D.

The Structure of Silver Crystals. L. VEGARD (*Phil. Mag.*, 1916, [vi], **31**, 83—87).—Röntgen-ray analysis of the structure of silver crystals has shown that the atoms are arranged according to the simple face-centred lattice, which is identical with the arrangement found by Bragg (A., 1914, ii, 775) for crystals of copper.

H. M. D.

Investigations in the Field of Silicate Chemistry. IV. Data for the Meta- and Ortho-silicates of the Bivalent Metals: Glucinum, Magnesium, Calcium, Strontium, Barium, Zinc, Cadmium, and Manganese. F. M. JAEGER and H. S. VAN KLOOSTER (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 896—913. Compare A., 1914, ii, 363, 810).—The silicates were prepared synthetically by heating together pure finely-powdered quartz with the pure oxides or carbonates of the metals in iridium-free platinum crucibles and repeating the process after the addition of silica or metallic oxide until the finely-ground product was found by

analysis to be of the right composition. The melting points, densities, and refractive indices were measured, and the data are given in the following summary: glucinum metasilicate, m. p. >1750°; strontium metasilicate, m.p. 1578°, D_4^{25} 3·652, n_1 1·620, n_2 1·590; strontium orthosilicate, m. p. >1750°; barium metasilicate, m. p. 1604°, D_4^{25} 4·435, n_1 1·670, n_2 1·667; barium orthosilicate, m. p. >1750°; zinc metasilicate, m. p. 1437°, D_4^{25} 3·52, n_1 1·623, n_2 1·616; zinc orthosilicate, m. p. 1509·5°, n_1 1·719, n_2 1·697; cadmium metasilicate, m. p. 1242°, D_4^{25} 4·928, n_1 and n_2 >1·739; cadmium orthosilicate, m. p. circa 1252°, n_1 and n_2 >1·739; manganese metasilicate, m. p. 1273°, D_4^{25} 3·716, n_1 1·739, n_2 1·733; manganese orthosilicate (tephroite), m. p. 1290—1300°, D_4^{25} 4·044, n_1 and n_2 >1·739.

By comparison with previous data for the calcium and magnesium silicates it is found that the m. p. of calcium, strontium, and barium metasilicates increase regularly with increasing atomic weight of the metal, whilst the data for the metasilicates in the series magnesium, zinc, cadmium show a regular decrease with increase in the atomic weight. H. M. D.

Action of Boiling Acetic, Propionic, and Butyric Acids on Aluminium, with a Note on the Action of Formic and Some Higher Acids. RICHARD SELIGMAN and PERCY WILLIAMS (*J. Soc. Chem. Ind.*, 1916, **35**, 88—93).—The corrosion of aluminium by the acids of the acetic acid series is conditioned largely by the concentration of the acid in question. The rate of dissolution falls as the strength of the acid increases, a 99% acetic acid having only about one-tenth of the action of a 90% acid. With a perfectly anhydrous acid, however, the rate of dissolution increases a hundredfold. In these circumstances a crystalline acetate is formed containing more acetic acid than the least basic acetate hitherto described, and the increased action is apparently due either to the smaller protection afforded to the surface of the metal by the crystalline acetate than by the basic gelatinous acetate formed when moisture is present, or to the formation of a protective coating of oxide when water is present, which retards a normal high rate of dissolution of the metal in these acids. The behaviour of propionic and butyric acids is analogous to that of acetic above described. Formic acid of 77% strength rapidly attacks aluminium, a crystalline formate being formed, which, unlike the other salts, is not decomposed by the water present into a gelatinous basic salt. All the above acids in a diluted form attack the metal rapidly, because the solubility of the basic salts increases rapidly as the strength of the acid falls. With stearic and other higher fatty acids, moisture also appears to play a part. Below 300° the metal is unattacked; above this temperature action is rapid, and continues when the temperature has fallen even to 100°. At this lower temperature, stearic acid attacks amalgamated aluminium, and it is considered that this is due to the fact that a protective coating of oxide cannot be formed in presence of the mercury. G. F. M.

Circulation of Manganese in Natural Waters. V. VINCENT (*Compt. rend.*, 1916, **162**, 259—261).—Manganese is present in

solution in natural waters in the form of manganese hydrogen carbonate. Of the three oxides, manganous oxide is most soluble in water saturated with carbon dioxide, then comes the sesquioxide, the least soluble being manganese dioxide. A humus solution only dissolves manganous oxide or manganese carbonate, being without action on the sesquioxide and the dioxide. The naturally occurring oxide being the sesquioxide, this explains the low content of manganese in natural waters, the drainage waters from the experimental field being found to contain only 0·01 mg. of manganese per litre. The action of the commonly used fertilisers is much inferior to that of carbon dioxide in dissolving the manganese. W. G.

Action of Certain Chlorinated Hydrocarbons on Some Metals in the Presence of Moisture. SOSALE GARALAPURY SASTRY (*J. Soc. Chem. Ind.*, 1916, **35**, 94—95).—The corroding action of some of the technical chlorinated solvents on steel, iron, nickel, copper, aluminium, and lead was studied by boiling thin strips of metal in the various solvents for periods of ten hours and determining the loss in weight. Di- and tri-chloroethylene were found to cause the least corrosion in all cases, the action of tetra- and penta-chloroethane being much more pronounced, and, in the case of aluminium, the metal was completely destroyed, probably owing to the dissociation of the solvents into hydrogen chloride and chloroethylenes. The corrosive action is naturally increased in the presence of moisture. Towards the chlorinated ethanes nickel was in general the most resistant. Carbon tetrachloride had no measurable corrosive action, under the above experimental conditions, on any of the metals except copper and lead, and then only to a very slight extent. G. F. M.

Synthesis of Nickel Arsenides. A. BEUTELL (*Centr. Min.*, 1916, 49—56).—Comparative experiments were made by heating metallic nickel, cobalt, and smaltite in an atmosphere of arsenic at temperatures of 300—450° (compare A., 1916, ii, 142). Owing to the fact that a skin of arsenide forms on the surface of the material, it is necessary to continue the heating for many weeks and to re-powder the material several times before a condition of equilibrium is attained. At 400° there is no marked difference between the behaviour of nickel and cobalt, but at 450° the sintering of the nickel arsenide causes the reaction to cease, whilst with cobalt it proceeds slowly. The highest nickel arsenide obtained was $NiAs_2$, and there are no well-marked stages in the process between NiAs and $NiAs_2$. L. J. S.

Amphoteric Metallic Hydroxides. III. JOHN KERFOOT WOOD and VERA KATHLEEN BLACK (T., 1916, **109**, 164—171. Compare T., 1908, **93**, 411; 1910, **97**, 878).—In view of the inconclusive nature of the evidence afforded by previous observations on the acidic character of chromium hydroxide, further experiments have been made, in which chromic hydroxide, prepared from chrome alum by precipitation with ammonia, was exposed to the action of solu-

tions of sodium hydroxide at 25° for prolonged periods of time. In these circumstances the solutions slowly acquired a yellow colour, due to the formation of chromate. The observation is considered to indicate the amphoteric character of chromium hydroxide, the chromate resulting from the oxidation of the dissolved chromite. In support of this view, it was found that no chromate was formed when the sodium hydroxide solution was made up with freshly boiled water and the containing vessel was completely filled.

The rate of formation of chromate increases with the concentration of the alkali solution, but these are not proportional, and from this the authors draw the conclusion that the chromium hydroxide behaves as a polybasic acid.

Attempts to measure the degree of hydrolysis of chromic chloride solutions by the ester catalysis method were unsuccessful.

H. M. D.

Experiments on the Separation of Vanadium from Crude Sodium Uranate. H. H. BARKER and H. SCHLUNDT (*J. Soc. Chem. Ind.*, 1916, **35**, 175; from *Met. and Chem. Eng.*, 1916, **14**, 18—23).—The following methods are suggested for the direct separation of vanadium from the crude sodium uranate obtained as a by-product in the extraction of radium from carnotite: (1) On a laboratory scale vanadium was completely volatilised by the action of gaseous hydrogen chloride, and a residue was obtained consisting of sodium uranate and chloride and uranyl chloride, from which 59—64% of the total uranium was recovered as pure oxide by boiling with ammonium chloride and igniting the ammonium uranate produced. By proper regulation of temperature vanadium could probably be removed directly and quantitatively from carnotite by this method. (2) By heating the crude uranate with ammonium chloride and sufficient water to form a paste, the vanadium content was reduced from 8·5 to less than 0·5%, and the uranium was partly converted into oxide. (3) By dissolving the crude uranate in the least possible quantity of dilute hydrochloric or nitric, or, in some cases, sulphuric acid, and boiling the solution, the vanadium was completely co-precipitated with about 13% of the uranium, and pure uranium oxide was obtained by adding ammonia to the filtrate and igniting the ammonium uranate obtained. By this means from 58% to 79% of the total uranium was recovered as pure oxide when dilute hydrochloric or nitric acid was employed.

G. F. M.

Atomic Weight of Bismuth. W. ŒCHSNER DE CONINCK and GÉRARD (*Compt. rend.*, 1916, **162**, 252).—The bismuth used was freed from arsenic and sulphur by fusing it several times with potassium nitrate. It was then converted into its chloride, which was used for the determination. The pure chloride was weighed, reduced by pure hydrogen, and the resulting metal weighed. The atomic weight was calculated from these two weights, and the mean of four determinations gave the value 208·50 for the atomic weight of bismuth.

W. G.

Subhaloid Compounds of Some Elements. II. So-called Bismuth Subchloride and Sub-bromide. L. MARINO and R. BECARELLI (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 625—631. Compare A., 1913, ii, 227; A., 1915, ii, 770).—When mixtures of bismuth with proportions of bismuth trichloride or tribromide varying from 5% to 85% are fused in the sealed tubes previously used by the authors, two layers are obtained above 320°, the upper one being black and the lower white with a metallic lustre. Lowering of the temperature results in the formation: (1) from one of the two strata, of a crystalline product melting over the range 270—305° for the bromide or 270—320° for the chloride; at about 240° this is transformed into two other products (*a*) m. p. about 260°, and (*b*) m. p. 270—305°, and 270—320° in the two cases; (2) from the other stratum the eutectic Bi–$BiBr_3$, m. p. about 200°, or Bi–$BiCl_3$, m. p. about 180°. The authors regard the crystalline product as a series of mixed crystals formed with very little development of heat. The melting points of these series are in all cases higher than those of the components, but it has not been found possible to establish exactly the limits of their region of existence or to ascertain if the equilibrium curve exhibits a maximum, since the experimental results are complicated by the sublimation of the tribromide or trichloride. Eggink's conclusions (A., 1908, ii, 1043) are regarded as erroneous. T. H. P.

Subhaloid Compounds of Some Elements. III and IV. The So-called Bismuth Sub-bromide. L. MARINO and R. BECARELLI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 105—111, 171—177).—III. The experimental data obtained in the cryoscopic investigation of the system bismuth–bismuth tribromide (preceding abstract) are given.

IV. From all the upper layers formed in different mixtures of bismuth and bismuth bromide at 200°, there drops in greater or less quantity, according to the composition of the mixture, a liquid which, on cooling, forms the black, hygroscopic substance previously mentioned. For each of these strata there remains a crystalline network which melts between about 270° and 300—305°, and is regarded as a series of mixed crystals, which undergo transformation into a β-form and then into a γ-form with pronounced development of heat. The melting point of the γ-crystals is always above those of bismuth and bismuth tribromide, and on fusion and cooling they yield α-crystals of different composition, together with two liquid strata which reproduce this series of changes. At 153° bismuth tribromide undergoes transformation into the solid form. Eggink's conclusions (A., 1908, ii, 1043) appear to call for revision.

T. H. P.

Rapid Method of Converting Scrap Platinum into Chloroplatinic Acid. J. BISHOP TINGLE and ALFRED TINGLE (*J. Soc. Chem. Ind.*, 1916, **35**, 77).—The conversion of scrap platinum into chloroplatinic acid is facilitated by alloying it with some base metal, preferably zinc, by fusion under a layer of borax. The alloy is

treated with hydrochloric acid, which dissolves out most of the zinc and leaves the platinum as a finely divided black powder, which is almost instantly soluble in aqua regia. This solution contains some zinc, and is accordingly treated either with a rod of pure zinc to precipitate the platinum or with hydrogen sulphide, the precipitated platinum sulphide being washed and ignited. The residue of platinum obtained in either case is dissolved in aqua regia, excess of acid is expelled by evaporating to dryness, and the residue dissolved in water forms a solution of pure chloroplatinic acid.

G. F. M.

Mineralogical Chemistry.

Melting Points and Boiling Points of Mineral Sulphides, Selenides, and Tellurides of the Metalloids. L. H. BORGSTRÖM (*Jahrb. Min.*, 1916, i, Ref. 9—11; from *Öfversigt Finska Vetens.-Soc. Förh.*, 1915, **57**, Afd. A, No. 24, 1—13).—The method of determining the melting points of minerals from the heating and cooling curves necessitates the use of a considerable amount of material, whilst the microscopic method lacks accuracy. The author has made use of a method employed for organic substances, the substance being enclosed in a capillary tube of silica-glass and immersed in a transparent bath of fused salts (mixtures of sodium and potassium nitrates, sodium, potassium, and lithium chlorides, and sodium sulphate in various proportions according to the temperature required). The results obtained are tabulated below:

	Melting point.	Boiling point.
Realgar (AsS)	307—314°	589°
Orpiment (As_2S_3)	320—325	690
Stibnite (Sb_2S_3)	546—551	990 about
Bismuth-glance (Bi_2S_3)	717—720	—
Guanajuatite (Bi_2Se_3)	690	—
Tetradymite ($Bi_2[Te,S]_3$)	593—602	—
Molybdenite (MoS_2)	infusible	—
Kermesite (Sb_2S_2O)	516—518	—

A connexion is traced between the melting points and the geological occurrence of these minerals, those with higher melting points being found at greater depths in the earth's crust. L. J. S.

Alotrichite from Rio (Elba). FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1915, [v], **24**, ii, 501—503).—In addition to the numerous sulphates which have been observed in the ferriferous deposits of Elba, the author has now found two specimens of alotrichite collected at Rio. The mineral occurs in moderately compact

masses of fibrous structure, the fibres, which have an almost parallel arrangement, being white or faintly blue and of a silky lustre; D^{14} 1·901, hardness about 2·5. Analysis gives the figures:

SO_3.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	H_2O.	Total.
35·40	11·97	0·67	7·49	trace	43·80	99·33

which are in fairly satisfactory agreement with the formula $FeSO_4,Al_2(SO_4)_3,24H_2O$. The deficit of water is due to partial dehydration, which occurs at the ordinary temperature in a dry atmosphere, and the excess of sulphuric acid to the presence of ferric, aluminium, and calcium sulphates as impurities. The two specimens were accompanied by small crystals of pyrites and scales of hæmatite. It is considered probable that the angle of extinction of alotrichites varies with the content of iron, and possibly with that of water. T. H. P.

New Mineral Occurrences from the Tintic District, Utah. A. H. MEANS (*Amer. J. Sci.*, 1916, [iv], **41**, 125—130).—The following mineral species present in mixed ore samples were determined by qualitative tests: geocronite, adamite, daubreeite (?) ($2Bi_2O_3,BiCl_3,3H_2O$), as small, yellowish-brown rosettes of slender, hexagonal prisms with brilliant lustre, bismite (?) (Bi_2O_3), and jarosite. Bismutite (Bi_2O_3,CO_2,H_2O) occurs in the Victoria mine as thin, dark veinlets in an ore containing argentite, barytes, quartz, etc.; analysis, by R. C. Wells, of the mixed mass gave I. *Arseno-bismite*, a new bismuth arsenate, occurs in considerable amount in the Mammoth mine. The heavy, yellow, friable ore consists of a mixture of arseno-bismite, limonite, barytes, erinite, and mixite. Analysis II, by R. C. Wells, is of the heavy concentrate obtained by vanning. Deducting large amounts of impurities, the formula is deduced as $2Bi_2O_3,As_2O_5,2H_2O$. The material forms yellowish-green, crystalline aggregates; D 5·70:

	Bi_2O_3.	As_2O_5.	Fe_2O_3.	PbO.	CaO.	SO_3.	CO_2.	H_2O.	Insol.	Total.
I.*	18·07	0·05	0·92	0·31	0·76	0·58	2·48	—	66·10	96·99
II.†	28·17	10·59	3·88	1·12	0·62	0·46	—	2·52	49·92	99·14

* Also loss on ignition 3·57, Ag 4·15.
† Also Al_2O_3 0·44, CuO 0·12, MgO trace, P_2O_5 0·04, Sb_2O_3 1·26.

The above formula deduced from this analysis approximates to those of atelestite and rhagite. L. J. S.

Intumescent Kaolinite. W. T. SCHALLER and R. K. BAILEY (*J. Washington Acad. Sci.*, 1916, **6**, 67—68).—White, glistening lumps from Back Bone Mountain, Le Flore Co., Oklahoma, consist of minute, hexagonal crystals with refractive indices: α 1·561, β 1·563, γ 1·567. The results of analysis—SiO_2, 46·55; Al_2O_3, 38·90; H_2O, 14·04 = 99·49—agree very closely with the kaolinite formula. Loss of water at 145°, 0·09%; at 220°, 0·11%, and at 330°, 0·12%. The mineral only differs from ordinary kaolinite in the fact that it intumesces strongly before the blowpipe. L. J. S.

The Variable Composition of Melanochalcite. W. F. HUNT and E. H. KRAUS (*Amer. J. Sci.*, 1916, [iv], **41**, 211—214).—A lustrous, pitchy-black mineral occurring at Bisbee, Arizona, as a banded coating on massive cuprite and penetrated by thread-like veins of chrysocolla and malachite, closely resembles the melanochalcite of G. A. Koenig (A., 1903, ii, 156) from the same locality. It differs from this slightly in the colour of its brownish-black streak and in its sp. gr. of 4·704. It gave analysis I; Koenig's analysis is quoted under II:

	CuO.	SiO_2.	CO_2.	H_2O.	ZnO.	Fe_2O_3.	Total.
I.	88·94	4·31	1·78	4·48	0·12	0·22	99·85
II.	76·88	7·80	7·17	7·71	0·41	0·07	100·04

Analysis I is interpreted as a mechanical mixture of tenorite (68·6%), chrysocolla (20%), and malachite (11·4%); and II as a mixture of the same minerals in the respective amounts 30·8%, 30·8%, and 38·4%. This view is supported by a microscopical examination of the powdered mineral. Cold dilute acid dissolves the particles of malachite, leaving the tenorite and chrysocolla. Melanochalcite is therefore not a mineral species, but a mixture.

L. J. S.

Analytical Chemistry.

The Free Chlorine in Town Drinking Waters. G. A. Le Roy (*Compt. rend.*, 1916, **162**, 327—329).—Ten litres of the water under examination are placed in an enamelled metal vessel, which is immersed in a brine-bath kept below 0°, and the water is allowed to freeze until only about 200 c.c. are left, taking care not to stir the water or aerate it. The last 200 c.c. of water are poured off and examined for free chlorine by means of magnesium iodide and starch. The method can be made quantitative by accurately measuring the volumes of water and estimating the chlorine colorimetrically, and can be made more delicate by starting with a larger volume of water and leaving still only 200 c.c. after freezing.

W. G.

Rapid Method of Estimating Chloric Acid and Chlorates. R. L. Taylor (*J. Soc. Dyers*, 1916, **32**, 66—68).—The liberation of iodine from potassium iodide by chloric acid or chlorates is quantitative in the presence of moderate concentrations of hydrochloric acid, and a method for their estimation either alone or in presence of hypochlorites, as, for example, in bleaching powder, is based on this reaction. From one and a-half to two volumes of concentrated hydrochloric acid are added to the solution to be titrated, together with a few crystals of potassium iodide, and the liberated

iodine titrated with thiosulphate after diluting somewhat with water. The high concentration of hydrochloric acid does not affect the accuracy of the titration. G. F. M.

Water Analysis. II. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1916, **29**, 44—46. Compare A., 1915, ii, 173).—For the estimation of dissolved oxygen in water containing nitrites and organic matter, the water should be treated previously with a small quantity of sulphuric acid and a slight excess of calcium hypochlorite solution; the oxygen estimation is then carried out as usual by the manganous chloride method. Allowance is made for the effect of the excess of chlorine by treating a similar quantity of the water with the same quantities of sulphuric acid and calcium hypochlorite solution, then adding a crystal of potassium iodide, and titrating the liberated iodine. Total alkalis may be estimated by evaporating a definite quantity of water with the addition of barium carbonate, extracting the dry residue with successive quantities of hot water, and evaporating the filtered aqueous extracts to dryness with the addition of a drop of hydrochloric acid. The residue, consisting of potassium, sodium, and magnesium chlorides, is extracted with *iso*butyl alcohol to remove the magnesium chloride, then dried at 150°, and weighed. The potassium is estimated by dissolving the mixed alkali chlorides in one hundred times their weight of lithium hydrogen tartrate solution (0·5 gram of lithium carbonate and 2 grams of tartaric acid dissolved in 100 c.c. of water, the solution mixed with 50 c.c. of alcohol, and then saturated with potassium hydrogen tartrate), collecting the precipitated potassium hydrogen tartrate after the lapse of two hours, washing the precipitate with a small quantity of 30% alcohol saturated with potassium hydrogen tartrate, and titrating it with standard alkali solution.

Water supplies sometimes contain zinc owing to the water having been passed through "galvanised" iron pipes. Small quantities of zinc in water may be detected and their quantity estimated approximately by the following test: 100 c.c. of the sample are treated with 1 c.c. of 10% hydrochloric acid and 1 c.c. of hydrogen sulphide solution, and 5 c.c. of 15% ammonium acetate solution are then added. A turbidity develops almost immediately if the water contains 10 mg. of zinc per litre, whilst the turbidity is not seen until after the lapse of about one minute if only 2 mg. of zinc per litre are present. An equal volume of the water similarly treated, but without the ammonium acetate, serves as a comparison solution; this remains clear if the water contains up to 10 mg. of ferrous iron per litre, but it becomes turbid if ferric salts are present. Ferric salts, therefore, render the test untrustworthy. The zinc may also be estimated by a method described previously by the author (A., 1913, ii, 246). W. P. S.

Estimation of Sulphur in Zinc Blende. H. KOELSCH (*Chem. Zeit.*, 1916, **40**, 174).—The fusion method with sodium peroxide is recommended. A quantity of 0·625 gram of the blende, or 1·25 grams of roasted blende, is fused with 15 grams of sodium peroxide

in an iron crucible, cooled, the mass dissolved in about 150 c.c. of water, the solution nearly neutralised with hydrochloric acid, then diluted to 250 c.c., filtered, and the sulphuric acid is estimated in 200 c.c. of the filtrate by precipitation as barium sulphate. The presence of a small quantity of silica in the ore does not appreciably affect the results, and the latter agree with those found by fusion with a mixture of sodium carbonate and potassium chlorate.

W. P. S.

Estimation of Free Sulphur in Antimony Sulphides. A. HUTIN (*Ann. Chim. anal.*, 1916, **21**, 32—33).—For the extraction of free sulphur from various antimony sulphides the use of acetone is recommended in place of carbon disulphide, since the latter, when warm, is capable of converting antimony pentasulphide into the tetrasulphide. Owing to the slight solubility of sulphur in acetone, at least eight hours' extraction is necessary in order to obtain the whole of the free sulphur. W. P. S.

A New Method for the Analysis of Mixed and Spent Acids. L. WUYTS (*J. Soc. Chem. Ind.*, 1916, **35**, 149—151).—A modification of Schloesing's method suited for the estimation of nitric and nitrous acids in mixed and spent nitrating acid consists essentially in the conversion of the nitrogen into nitric acid by slowly dropping a known weight of the acids from a tap-funnel with a capillary stem, bent twice at right angles, into a boiling solution of ferrous chloride and hydrochloric acid contained in a Kjeldahl flask of about 200 c.c. capacity. The evolved gas is led by a delivery tube to the base of a graduated burette standing over water, care being taken that the water does not suck back into the flask owing to a slackening of the boiling. The weight of nitric acid is calculated either directly from the volume of nitric oxide obtained, or preferably by comparison with a standard tube of gas obtained by treating a known weight of pure sodium or potassium nitrate in a similar manner. The accuracy of the estimations is of the order of 0·1%, and seven or eight samples can be analysed per hour. G. F. M.

Detection of Nitrates in Presence of Organic Matter. ALFRED TINGLE (*J. Soc. Chem. Ind.*, 1916, **35**, 77—78).—The salicylic acid test for nitrates previously described (A., 1915, ii, 576) is modified as follows to admit of their detection in presence of organic matter: 2—5 c.c. of the reagent, consisting of a solution of 3 grams of salicylic acid in 100 c.c. of concentrated sulphuric acid, is gently warmed with the substance, and the charred mass extracted with 10 c.c. of water. The aqueous extract is shaken with an equal volume of ether, and the ethereal solution, which contains nitrosalicylic acid if nitrates were present, is shaken with aqueous ammonia, which assumes an orange colour, or with a 1% aqueous solution of ferric chloride, whereby a red coloration is slowly developed in the aqueous layer. Examples are given of the employment of the test to detect 0·1% of potassium nitrate in a saturated solution of sucrose and cellulose nitrate in a photographic film.

G. F. M.

Influence of Fluorspar on the Solubility of Basic Slag in Citric Acid. G. S. ROBERTSON (*J. Soc. Chem. Ind.*, 1916, **35**, 216—217).—The use of fluorspar in the manufacture of steel by the open-hearth process results in the production of a phosphatic slag of low citric acid solubility, performing the test in the usual way with one extraction only. By repeated extraction with 2% citric acid a much larger amount of phosphate is rendered soluble, and as the amounts of silica removed by the successive extractions bear no definite ratio to the phosphate, the latter does not appear to be in combination with silica in the slag, as is usually supposed. The results indicate that the citric acid test gives no idea of the solubility of the phosphate in fluorspar slags, and is worthless as a guide to its agricultural value as a fertiliser. G. F. M.

Solubility of Mineral Phosphates in Citric Acid. G. S. ROBERTSON (*J. Soc. Chem. Ind.*, 1916, **35**, 217—220).—Provided that sufficient time be given to the extraction, mineral phosphates are as completely soluble in 2% citric acid solution as is basic slag, and as a source of phosphoric acid for the plant they are doubtless just as valuable. In the majority of the rock phosphates examined, five extractions removed 90—100% of the phosphoric acid present. Small amounts of free lime or calcium carbonate appreciably decrease the solubility as judged by the citric acid test, but from the agricultural point of view there is absolutely no reason why the citric solubility should be used to judge of the phosphatic value rather than that in a dilute mineral acid. Fineness of grinding also considerably affects the total citric solubility of mineral phosphates, and in all cases but one, calcination caused a decrease in solubility.

G. F. M.

Estimation of Carbon Dioxide in Air by Haldane's Apparatus. ROBERT C. FREDERICK (*J. Soc. Chem. Ind.*, 1916, **35**, 96—99).—The use and construction of Haldane's apparatus comprising several modifications is described and figured in detail. The principal novelties include a special arrangement of taps to regulate the flow of air into the potash absorption bulb, a graduated scale on the stem of the potash bulb to enable larger quantities than 100 parts per 10,000 to be estimated, and a stand with pulley wheels and counterpoise to facilitate the manipulation of the mercury reservoir. For a complete description the original paper must be consulted.

G. F. M.

Carbonic Acid in Mineral Waters. RAMÓN LLORD Y GAMBOA (*Anal. Fis. Quim.*, 1916, **14**, 36—38).—A description of the results of investigations of the percentage of carbon dioxide in various mineral waters by different methods. A. J. W.

Estimation of Alkalinity of Water. F. W. BRUCKMILLER (*Chem. News*, 1916, **113**, 104—105).—The water is first titrated with $N/50$-sulphuric acid, using phenolphthalein as indicator; methyl-orange is then added and the titration continued. Ery-

throsin solution and chloroform may be used in place of methyl-orange in the second titration. If the alkalinity of the water is due to hydrogen carbonates alone, no coloration is obtained when phenolphthalein is added to the water, and the alkalinity towards methyl-orange is expressed as "bicarbonate" alkalinity. When the phenolphthalein titration is less than the methyl-orange titration, carbonates and hydrogen carbonates are present, and the alkalinity is due solely to normal carbonates if the two titrations give equal results. The presence of hydroxides causes the phenolphthalein titration to be greater than the methyl-orange titration. The quantities of carbonate, hydrogen carbonate, and hydroxide respectively (all expressed in terms of $CaCO_3$ per million parts of water) may be calculated from the results of the titrations. W. P. S.

Estimation of Free Alkali Hydroxide in Soap. F. H. NEWINGTON (*J. Soc. Chem. Ind.*, 1916, **35**, 95—96).—To obviate the sources of error and the difficulties which are attendant on the usual method of estimating alkali hydroxide in soap, namely, titration of an absolute alcoholic solution with standard acid, the following method is suggested: 10 grams of the sample are dissolved in 50 c.c. of freshly boiled, hot distilled water, and 50 c.c. of a hot saturated solution of sodium sulphate are added. The mixture is transferred to a separating funnel, which is lightly corked and placed in a hot-water oven until the soap separates out on the surface of a clear aqueous layer. The latter, which contains all the hydroxide originally present in the soap, is run off and titrated with $N/10$-sulphuric acid, using a 5% silver nitrate solution as a spot indicator on a porcelain plate. The end-point is attained when a brown precipitate of silver oxide is no longer formed; silicates, carbonates, etc., which may be present in the aqueous solution cause no confusion. G. F. M.

Potassium Metabisulphate. A. A. BESSON (*Chem. Zeit.*, 1916, **40**, 165—167).—If the salt has a normal composition, the quantity of sulphur dioxide present may be estimated either alkalimetrically or iodometrically, but the latter method is to be preferred, since the results obtained are not affected by the presence of other hydrogen salts. The weighed quantity of the sample should be treated directly with an excess of $N/10$-iodine solution, and the mixture then titrated with thiosulphate solution. The sulphur dioxide content of the commercial salt varies between 54·45% and 55·97% ($K_2S_2O_5$ requires 57·66%); sulphate is almost always present. Pure potassium metabisulphite does not smell of sulphur dioxide, but if exposed to air and moisture gradual decomposition takes place and an odour of sulphur dioxide is noticed.
W. P. S.

An Investigation of the Chromate Method for Separating the Alkaline Earths. HUBERT BRADFORD VICKERY (*Trans. Nova Scotian Inst. Sci.*, 1914–1915, **14**, 30—40).—Experiments have been made in order to ascertain the sensitiveness of the chromate method

of separating the alkaline earths and the best conditions for carrying out this process.

Comparative tests showing the minimum quantities of barium, strontium, and calcium which yield precipitates on the addition of the same quantity of ammonium carbonate, of potassium chromate, and of ammonium sulphate were made. Further tests were made in order to determine the minimum quantities of each of the alkaline-earth metals which could be detected in presence of relatively large quantities of the other two, when the separation is carried out in a normal manner. In presence of 200 mg. of calcium and strontium, the limiting quantity of barium which can be detected is 4 mg. With 200 mg. of barium and calcium, the limiting quantity of strontium is 15 mg., and with barium and strontium present in large excess, the limiting quantity of calcium was found to be about 1 mg. H. M. D.

Application of the Paper-pulp Filter to the Estimation of Calcium and Magnesium. S. L. Jodidi and E. H. Kellogg (*J. Franklin Inst.*, 1916, **181**, 217—232).—The use of paper-pulp filters for the separation of calcium oxalate and magnesium ammonium phosphate precipitates from the mother liquors has been found to yield very satisfactory results. The estimation of both calcium and magnesium requires much less time than when the separation is effected by the use of filter papers. H. M. D.

Method for the Analysis of Magnesium Chloride. L. Bourdet (*J. Pharm. Chim.*, 1916, [vii], **13**, 102—104).—If magnesium chloride is twice evaporated with nitric acid (D 1·4) and the residue then ignited at a bright red heat, all the hydrochloric acid is expelled and the residue will consist of magnesium oxide; the quantity of nitric acid used should be about three times the weight of the magnesium chloride. In cases where impurities are present in the magnesium chloride, the magnesium, chlorine, sulphuric acid, ammonia, etc., must be determined separately. The total amount of impurity is found approximately by the difference between the weight of the ignited residue obtained as described and the sum of the weights of the magnesium oxide, ammonia (if present), insoluble substances, and the excess of chlorine (that is, the chlorine not combined with the magnesium). W. P. S.

Estimation of Zinc by Electrolysis. F. Chancel (*Bull. Soc. chim.*, 1916, [iv], **19**, 59—63).—In order to obtain a satisfactory deposit of zinc it is necessary to have a uniform current density on the cathode and to ensure that the acidity of the solution should be constant. The estimations were made with the small platinum cathodes in the apparatus previously described (compare A., 1913, ii, 236), the cathode being first coated with mercury or copper, preferably mercury. The solution for electrolysis was prepared as follows: About 0·3 gram of the zinc was dissolved in 1·5 grams of sulphuric acid and 2 grams of nitric acid, the nitric acid then being evaporated. The residue was taken up with water, neutralised

with aqueous ammonia, and then 0·25 c.c. of *N*-sulphuric acid was added, followed by 0·2 gram of sodium formate for every decigram of zinc present. A current of 4—5 amperes was used, and the electrolysis took three hours. Provided that a sufficiently thick deposit of mercury is obtained, the deposition of the zinc is complete, the results being, on the average, 0·2% too high.

For the analysis of brass, the solution in nitric acid and precipitation of the copper are carried out in the usual manner, the filtrate from this being first evaporated with sulphuric acid, then saturated with ammonia to precipitate the iron, the excess of ammonia boiled off, and then 0·25 c.c. of *N*-sulphuric acid and the requisite amount of sodium formate added. W. G.

Electro-analysis of Copper without Platinum Electrodes. J. GUZMÁN and T. BATUECAS (*Anal. Fis. Quim.*, 1916, **14**, 38—47). Continuing their investigations of the electro-deposition of copper without platinum electrodes, the authors have employed an anode of graphite and a cathode of copper for the estimation of copper dissolved in hydrochloric, nitric, and sulphuric acids, and also in presence of arsenic, antimony, and tin. A. J. W.

Action of Mercuric Salts on Aluminium Foil. Application of the Reaction to the Detection of Mercury in Chemical Analysis and Toxicology. ST. MINOVICI and EM. GROZEA (*Bull. Sci. Acad. Roumaine*, 1915–1916, **4**, 227—230).—A solution containing mercuric chloride, when allowed to dry on aluminium foil, gives rise to a dendritic structure resembling that produced by calcium nitrate on damp walls. This reaction is not prevented by the presence of various other substances, and may be conveniently employed as a test for mercury, especially in toxicological investigations. S. B. S.

Action of Oxidising Agents on Cerous Salts. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 37—43. Compare A., 1907, ii, 467; 1910, ii, 779).—The oxidation of cerous salts by permanganate or by persulphates has been investigated (compare Muthmann and Weiss, A., 1904, ii, 406).

A solution containing not more than 1% of cerous sulphate and not less than 25% of sulphuric acid is readily oxidised by potassium permanganate in the hot, ceric sulphate being formed: $5Ce_2(SO_4)_3 + 2KMnO_4 + 8H_2SO_4 = 10Ce(SO_4)_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$; if 30% of sulphuric acid is present, the oxidation proceeds rapidly even in the cold. This method is, however, unsuitable for the volumetric estimation of cerium, since the yellow colour of the ceric sulphate renders the end-point indefinite.

If to a solution of a cerous salt are added excess of iodic acid and then sufficient nitric acid to dissolve the cerous iodate precipitated, complete and rapid oxidation to ceric iodate is effected by permanganate in the hot: $5Ce(IO_3)_3 + KMnO_4 + 5HIO_3 + 3HNO_3 = 5Ce(IO_3)_4 + KNO_3 + Mn(NO_3)_2 + 4H_2O$. This reaction cannot be employed for the volumetric estimation of cerium, since after com-

plete oxidation of the latter, reduction of the permanganate is continued, although more slowly, by the manganous salt formed. It does, however, serve for the quantitative separation of cerium from the other elements of its group, for instance, lanthanum, which form iodates soluble in dilute nitric acid and form compounds of only one type.

Permanganate is reduced even in the cold by a solution of cerous phosphate in excess of phosphoric acid, a bulky, white, gelatinous precipitate being formed which contains all the cerium as basic ceric phosphate, the ratio $Ce:P_2O_5$ being about 4:3. Since the supernatant liquid remains colourless, this reaction may be employed for the estimation of cerium, the procedure being as follows.

The cerous solution is diluted, where necessary, so as to contain not more than 0·1 gram of cerium per 100 c.c. To 100 c.c. of the liquid are added 20 c.c. of phosphoric acid solution (D 1·35) and then, drop by drop, decinormal permanganate solution until the precipitate acquires a faint rose-red colour. The liquid is next heated on a water-bath and the addition of permanganate continued until the supernatant liquid assumes a pale pink colour persistent in the hot.

This method gives good results even when the cerium is accompanied by other rare-earth elements; the quantity of phosphoric acid added should be sufficient to keep these elements in solution, even in the hot. If thorium is present, addition of phosphoric acid produces a precipitate of basic thorium phosphate, which is but slightly soluble in acids, but the presence of this precipitate does not disturb the oxidation of the cerous phosphate. Further, the titration is not affected by small proportions of manganous salts, whereas no volumetric method hitherto known is applicable when the cerium is accompanied by manganese.

The investigations of von Knorre (A., 1898, ii, 311), Witt and Theel (A., 1900, ii, 403), and Meyer and Marckwald (A., 1901, ii, 21) show that persulphates oxidise cerous salts in the hot, but not in the cold. The author finds that, if a little silver nitrate is added to a solution containing an alkali persulphate and cerous nitrate or sulphate, oxidation of the cerous salt by the persulphate commences immediately and proceeds until all the cerium is converted into ceric salt, which forms a yellow solution or a precipitate, according as the liquid is acid or neutral. The catalytic action of the silver depends on its conversion by the persulphate from the univalent to the bivalent form. This reaction serves for the purification of a crude cerium salt, since in neutral solution any other rare-earth metals remain dissolved, whilst almost the whole of the cerium is precipitated as basic salt. T. H. P.

Crum's and Marshall's Tests for Manganese. LEONARD DOBBIN (*J. Soc. Chem. Ind.*, 1916, **35**, 80—81 *).—The author points out that the credit for the application of the oxidation of manganese salts to permanganic acid by means of lead peroxide and nitric acid as a qualitative test for manganese, which has been variously ascribed

* and *Chem. News*, 1916, **113**, 133—135.

to Crum, Volhard, and Hoppe-Seyler, properly belongs to the former of those investigators. The modification of this test, using a persulphate in presence of sulphuric or nitric acids and a drop of silver nitrate solution as the oxidising agent, whereby 0·001 mg. of manganese in 0·5 c.c. of water could be detected, was suggested by Marshall (A., 1901, ii, 350), and not by Walters, to whom many writers have given the credit. G. F. M.

Estimation of Toluene, and the Application of the Method to Benzene and Xylene. HUGH W. JAMES (*J. Soc. Chem. Ind.*, 1916, **35**, 236—240).—Details are given of a method for the estimation of toluene in naphthas and crude benzols depending on a determination of the volume of the fraction obtained between two definite temperatures by the distillation under specified conditions of the mixed hydrocarbons which have been previously separated into two parts by a double fractionation of the original naphtha, the one part boiling below 110·6°, and the second between 110·6° and 140°. Each of the latter fractions is distilled from a 150—180 c.c. flask with a 5-inch neck and side delivery-tube at the rate of 2 drops per second, and the fractions are collected at 85°, 90°, 95°, 100°, and 108° for the first part, and 115°, 120°, 125°, 130°, and 137° for the second part. Tables are given showing the percentage volumes of mixtures of benzene, toluene, and xylene in known proportions which distil between these temperatures, and from the observed percentage the amount of toluene in the fraction undergoing distillation is directly read off. Benzene may be taken as the difference between the total volume of the fraction up to 110·6° and its toluene content, and xylenes the corresponding difference in the second fraction, 110·6—140°. The results have an accuracy of the order of 1%. For the estimation of toluene in tar a preliminary tar distillation must first be undertaken, details of which are given. G. F. M.

Solubility of Naphthalene in Ammonia; Cause of Naphthalene Stoppages in Pipes. SIEGFRIED HILPERT (*Zeitsch. angew. Chem.*, 1916, **29**, 57—59).—The following table shows the solubility of naphthalene in ammonia solution and in ammonia, the results being expressed as gram per 1000 grams of solution:

% NH_3.	0.	5.	10.	25.	100.
At 0° ...	0·019	0·030	0·042	0·064	33·0
At 25° ...	0·030	0·044	0·074	0·162	120·0

When the ammonia contains 2% of pyridine the solubility of naphthalene at 0° increases to 0·082, and at 25° to 0·245. Phenol does not affect the solubility. If carbon dioxide is passed into 25% ammonia containing naphthalene in solution, the greater part of the latter is precipitated. During the distillation of ammonia containing naphthalene, the condenser tubes, etc., should be kept at a temperature not lower than 30°, otherwise the naphthalene will condense in the tubes. For the estimation of naphthalene in ammonia the picrate method is recommended. The ammonia is cooled in a freezing mixture, neutralised gradually with sulphuric

acid, and distilled, about 30 c.c. of distillate being collected. The naphthalene is extracted from the distillate and condenser with ether, and an excess of *N*/20-picric acid solution is added to the ethereal solution. After two minutes the ether is evaporated under reduced pressure, the residue cooled in ice-water, the precipitate collected on a filter, washed with 5 c.c. of ice-water, and titrated with *N*/10-sodium hydroxide solution, using litmus as indicator.

W. P. S.

Lewis and Benedict Method for the Estimation of Blood Sugar. VICTOR C. MYERS and CAMERON V. BAILEY (*J. Biol. Chem.*, 1916, **24**, 147—161).—See this vol., i, 300.

The Presence in Industrial Sugars of Reducing Substances Other than Invert-sugar. L. MAQUENNE (*Compt. rend.*, 1916, **162**, 277—282).—Artificial mixtures of pure sucrose and pure invert-sugar can be readily analysed, and the amounts of each sugar present accurately determined by the method already described (compare this vol., ii, 56, 156), working either at 65° or 100°, or with boiling solutions. Working with commercial sugars, however, the reducing effect obtained with boiling solutions is much greater than when the estimation is made at 65°. The author considers that this difference is due to the presence of reducing substances other than invert-sugar in the commercial sugars, the difference being an approximate measure of the amount of these substances present.

W. G.

Recovery of Copper Sulphate from the Filtrates Obtained in the Gravimetric Estimation of Sugars with Fehling's Solution. KRUMHAAR (*Chem. Zeit.*, 1916, **40**, 174).—The alkaline copper solution is heated to boiling, a quantity of dextrose solution is added sufficient to precipitate all the copper as cuprous oxide, and the latter is collected and washed. The cuprous oxide is then heated with hydrochloric acid and oxidised by the addition of hydrogen peroxide; when the oxidation is complete, the solution no longer becomes turbid on dilution with water. The solution is now evaporated, the hydrochloric acid expelled by a second evaporation with sulphuric acid, the copper sulphate is dissolved in a small quantity of boiling water, the solution filtered, and poured into three times its volume of 96% alcohol. The sulphate is thus precipitated in the form of fine crystals, which are collected on a filter, washed with alcohol, and dried.

W. P. S.

Use of Enzymes and Special Yeasts in Carbohydrate Analysis. WILLIAM A. DAVIS (*J. Soc. Chem. Ind.*, 1915, **35**, 201—211).—Processes based on the differential behaviour of enzymes in the hydrolysis of carbohydrates are described for the estimation of individual sugars and starches in plants or other carbohydrate mixtures. Thus the selective hydrolysis exerted by invertase (from autolysed top yeast) and melibiase (from autolysed bottom yeast) is utilised for the estimation of raffinose, the former preparation converting it into melibiose and lævulose, and the

latter into galactose, dextrose, and lævulose, whence by determining the difference polarimetrically a measure of the raffinose present is obtained. The use of invertase preparations for the estimation of sucrose is recommended in preference to hydrolysis by citric or hydrochloric acid, since the presence of sodium acetate, derived from the lead acetate used in clarification, exerts an inhibitive action on the acid hydrolysis. Maltose cannot be estimated accurately by acid hydrolysis in presence of sucrose or lævulose. By using a maltase-free yeast, such as *Saccharomyces marxianus* or *S. exiguus*, however, every trace of dextrose, lævulose, or sucrose can be fermented away by a three to four weeks' incubation at 25°, and the maltose then estimated by the residual reducing power. The estimation of starch in plant material by acid hydrolysis is likewise vitiated by the pentosans, hemicelluloses, etc., present which may give reducing sugars which count as dextrose. Hydrolysis by taka-diastase at 38—40° results in the quantitative conversion of the starch into a mixture of maltose and dextrose. Full details for the carrying out of the above-cited methods are given in the paper. G. F. M.

Detection of Glycuronic Acid in Urine. H. ROGER (*J. Pharm. Chim.*, 1916, [vii], **13**, 119—120).—Five c.c. of the urine are treated with 0·2 c.c. of ammonia and 2 c.c. of lead acetate solution, a quantity of 1% ammonia is added, and the mixture subjected to centrifugal action. The sediment is separated, washed with 1% ammonia, then mixed with 5 c.c. of water, and treated with 0·5 c.c. of a 1% alcoholic naphtharesorcinol solution. The mixture is now acidified with 5 c.c. of concentrated hydrochloric acid, heated for fifteen minutes in a boiling water-bath, cooled, and shaken with 10 c.c. of ether. If the urine contains glycuronic acid, the ethereal layer shows a violet coloration; in the absence of glycuronic acid the ether is coloured faint red. W. P. S.

Use of Soluble Ferments in the Estimation of Urea. MODESTO MAESTRE IBÁÑEZ (*Anal. Fis. Quim.*, 1916, **14**, 28—35).—An account of results obtained in the estimation of urea by Marshall's urease method. A. J. W.

Estimation of Urea by the Urease Method. DONALD D. VAN SLYKE and GLENN E. CULLEN (*J. Biol. Chem.*, 1916, **24**, 117—122. Compare Fiske, this vol., ii, 119).—The use of a slower rate of aeration in driving the ammonia over into the standard acid, as recommended by Fiske, is considered unnecessary if the authors' original directions are strictly adhered to. The substitution of a saturated solution of potassium carbonate for the solid substance is desirable, and the authors emphasise the necessity for applying corrections for traces of ammonia in the reagents employed. H. W. B.

Quantitative Estimation of Urea. C. P. MOM (*Chem. Weekblad*, 1916, **13**, 72—75).—A method for the estimation of urea

in urine. The urea is converted into ammonium carbonate by the action of a culture of *Urobacillus Pasteurii*, and the carbonate estimated volumetrically. A. J. W.

Use of Nickel Hydroxide in Tannin Estimation. PURAN SINGH and T. P. GHOSE (*J. Soc. Chem. Ind.*, 1916, **35**, 159—160).—Instead of the nickel hydroxide paste as originally proposed (A., 1911, ii, 946), the substance is preferably used in the form of dry powder, washed free from sulphates with hot water, and finally with water containing a trace of tannic acid. The method is considered as trustworthy as the hide powder method. G. F. M.

Limits of Sensibility of the Colour Reactions of Proteins and Peptonising Enzymes. M. A. RAKUZIN, (MLLE.) EK. M. BRAUDO, and (MLLE.) G. F. PEKARSKAJA (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2051—2056).—A number of proteins of different types and also various proteolytic enzymes have been examined to ascertain which of the following colour reactions each gives and with what sensitiveness: the biuret, Millon's, Liebermann's, Adamkiewicz's, the xanthoprotein, Molisch's, Pettenkofer's, and Ostromisslenski's (A., 1915, ii, 602). The compounds examined were egg-albumin, peptone from egg-albumin, α- and β-gelatins, chondrin, elastin, casein, nucleic acid, nuclein, agar-agar, gluten, pepsin, trypsin, diastase, and pancreatin.

Only egg-albumin, its peptone and its adsorption products (compare Rakuzin, A., 1915, i, 1015), give all the above reactions. Casein from cows' milk (nucleo-albumin) and nutrose (sodium caseinate) give all except Liebermann's reaction. α-Gelatin gives only the biuret, Molisch's, and Ostromisslenski's reactions, and chondrin gives these and also the xanthoprotein reaction. Agar-agar gives only Molisch's and Pettenkofer's reactions. Molisch's reaction is given by all the above proteins and enzymes. Elastin gives only the biuret and Molisch's reactions. It is noteworthy that the sclero-proteins, chondrin, gelatin, and elastin, do not give Millon's reaction, although, according to Abderhalden, elastin yields 0·34% of tyrosine. The biuret reaction is given by all the proteins except nucleic acid and agar-agar, and Liebermann's and Adamkiewicz's reactions are given only by egg-albumin and its peptone.

Pepsin, which approximates to the proteins in elementary composition, gives only Molisch's reaction. Trypsin, on the other hand, gives the biuret, xanthoprotein, and Molisch's reactions; diastase and pancreatin give the biuret and Molisch's reactions. None of the four enzymes gives Pettenkofer's reaction, and neither pepsin nor trypsin gives Ostromisslenski's reaction.

The most sensitive of the protein reactions is that of Millon, which detects 1 part of protein per 13,560 of solution. Any one reagent is differently sensitive towards different proteins, in dependence on the varying proportions of the amino-acids present. Of the reactions for tryptophan, that of Adamkiewicz is more sensitive than that of Liebermann. T. H. P.

General and Physical Chemistry.

The Spectra of Some Intermetallic Compounds. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1915, **92**, 76—80).—The arc spectra of some alloys in air have been compared with those of their component metals. It is found that the spectrum of the alloy Cu_3Sb is the sum of the spectra of copper and antimony. The compound Cu_2Zn_3 also gives a spectrum which is the sum of those of copper and zinc. It is therefore to be assumed that these compounds are fully dissociated in the state of vapour. On the other hand, the spectra of the compounds Mg_3Sb_2, Bi_2Mg_3, and Mg_2Sn show slight differences in the relative intensities of different lines, and the reversal of the magnesium line 285·2 is favoured by bismuth and tin, although not by antimony. The spectroscopic method is not very suitable for the detection of intermetallic compounds (compare Berry, A., 1912, ii, 161; Wartenberg, A., 1915, ii, 226).

C. H. D.

The High Frequency Spectra (K Series) of the Elements, Chromium to Germanium. MANNE SIEGBAHN and WILHELM STENSTRÖM (*Physikal. Zeitsch.*, 1916, **17**, 48—51).—Measurements have been made of the wave-lengths of the four lines in the high-frequency spectra of chromium, manganese, iron, cobalt, nickel, copper, zinc, and germanium. The results obtained confirm the relation pointed out by Moseley, that the square root of the frequency of corresponding spectral lines is a linear function of the atomic number.

H. M. D.

Absolute System of Colours. WILHELM OSTWALD (*Zeitsch. physikal. Chem.*, 1916, **91**, 129—142).—A theoretical paper in which a method of defining the colour of any substance is discussed. It is held that a colour depends on the absolute dimensions of three variables—tone, brightness, and purity. A method of estimating these three factors is outlined.

J. F. S.

Foundation of a Scientific Theory of Pigments. I. The Fundamental Properties of Pigments and the Size of the Particles. WILHELM OSTWALD (*Kolloid Zeitsch.*, 1915, **16**, 1—4).—Attention is directed to the fact that the processes involved in the manufacture and application of paints are almost wholly empirical, and that no attempt seems to have been made to lay the foundations of an exact scientific treatment of the problems which this branch of industry presents.

The paper deals mainly with the influence of the size of the pigment granules on the chief properties, which are defined as colour. covering power, and effectiveness (Ausgiebigkeit). The colour is determined by the selective absorption, and the covering power, which depends on the scattering of the incident light, is

determined essentially by the refractive index of the pigment. As a measure of the covering power, the author suggests the maximum number of cm.[2] of surface which can be covered by 1 gram of pigment so that the underlying surface is invisible. The effectiveness, measured by the number of grams of white pigment with which 1 gram of the coloured pigment must be mixed before the colour of the latter begins to disappear, is determined by the magnitude of the coefficient of light absorption.

The influence of the size of the particles on the colour of many substances has already been examined in some detail, and the observed changes in colour have been explained satisfactorily on a physical basis.

In regard to covering power, it seems that this increases to a maximum with diminution in the size of the particles, and decreases again when the size of the particles approaches the wave-length of visible light rays. Pigments which consist of smaller particles than this have no scattering power towards light, and the covering power approximates to zero.

The effectiveness of a pigment is well known to increase with the fineness of subdivision, and in general no maximum is to be expected, as the size of the particles is continuously diminished. The effectiveness appears to be greatest when the degree of fineness is that corresponding with molécular dispersity. H. M. D.

The Relation of Position Isomerism to Optical Activity. X. The Menthyl Alkyl Esters of Phthalic Acid and its Nitro-derivatives. JULIUS BEREND COHEN, DAVID WOODROFFE, and LEONARD ANDERSON (T., 1916, **109**, 222—235).—Esterified by the Fischer-Speier method, 3-nitrophthalic acid gives mainly the β-ester, in which the alkyl group is remote from the nitro-group, whereas the anhydride gives mainly the α-ester. This was compared with the case of camphoric acid and its anhydride, but here it was found that the same product, the *ortho*-alkyl ester, was obtained by both methods, the *allo*-alkyl ester having to be prepared by half hydrolysis of the normal ester. Monobromosuccinic acid yielded by treatment with alcohol and hydrogen chloride a product differing from the mono-alkyl ester obtained from the anhydride and alcohol, as was shown by converting both into alkylmenthyl esters. An attempt to discriminate between the latter, however, by comparison of their rotations with those of corresponding nitrophthalic esters leads to inconsistencies. The effect on the rotation of menthyl methyl phthalate of the introduction of a nitro-group, firstly, in the position adjacent to the carboxymenthyl group, and, secondly, in that adjacent to the carboxymethyl group, has been studied. The rotation is raised in both cases, but to the greater extent when the nitro-group is in the position remote from the menthyl group. As the weight of the alkyl group increases the rotation diminishes, so that menthyl hydrogen phthalate has a higher rotation than menthyl methyl phthalate, but a minimum rotation is reached at menthyl *iso*amyl phthalate, after which, with increase of weight of the alkyl radicle, the rotation begins to rise.

A similar diminution of rotation is noticeable for the α-menthyl β-alkyl 3-nitrophthalates, whereas, in this respect, the β-menthyl α-alkyl 3-nitrophthalates show no particular regularity.

T. S. Pa.

The Effect of Light on Solid Silver Chloride and Bromide. Richard Lorenz and K. Hiege (*Zeitsch. anorg. Chem.*, 1915, **92**, 27—34).—Colloidal metallic 'fogs' are usually prepared by fusing salts in contact with the corresponding metals. The silver haloids also form fogs when the solid salts are exposed to light. Optically clear crystals of silver chloride and bromide, purified by the method previously described (A., 1915, ii, 260), become more or less opaque and dark in colour when exposed to a beam of light, but remain at first optically clear, the beam being invisible. Later, the surface at which the beam enters becomes brown, and particles, visible in the ultramicroscope, become visible. The particles grow rapidly, and will continue to grow if the crystal is removed from the light and heated at 350°. Heating in the absence of light does not produce particles. The growth of the particles is accompanied by a diminution of the coloration in their immediate neighbourhood. The effect is evidently due to the separation of metallic silver in a colloidal form, growing in size as the illumination is continued.

These facts strongly support the view that the latent photographic image consists of colloidal silver in ultramicroscopic form.

C. H. D.

Action of Light on Mixtures of Potassium Ferrocyanide and *p*-Nitrosodimethylaniline. W. Gallenkamp (*Chem. Zeit.*, 1916, **40**, 235).—Mixtures of potassium ferrocyanide and *p*-nitrosodimethylaniline solutions, originally yellow, develop a green colour on exposure to light. The change is very rapid even in diffused light, and appears to be an indirect photochemical catalysis, since after only a very short exposure the change slowly continues in the dark, whilst solutions prepared and kept in darkness remain yellow. The green colour is reconverted to yellow by heating the solution to the boiling point, but appears again on further exposure to light. Decomposition of the nitroso-compound by potassium nitrite or boiling potassium hydroxide results in the permanent destruction of the green colour. The author is of opinion that it is due to the production of colloidal Prussian-blue from the ferrocyanide under the influence of a catalyst generated from the nitroso-compound.

G. F. M.

Interaction of Hydrogen and Chlorine under the Influence of α-Particles. Hugh Stott Taylor (*J. Amer. Chem. Soc.*, 1916, **38**, 280—285).—A recalculation of results and a reconsideration of conclusions previously published (A., 1915, ii, 80).

J. F. S.

The Absorption and Diffusion of High Speed Cathode Rays (β-Rays) in Gases and Vapours. Einar Friman (*Ann. Physik*, 1916, [iv], **49**, 373—418).—Measurements have been made of the

absorption of the high-speed β-particles emitted by uranium-*X* in various gases and vapours. In particular, attention was directed to the elimination of errors resulting from the special design of the apparatus and from the diffusion of the rays. The actual procedure involved measurements in which the pressure of the absorbing gas was varied and others in which the distance between the source of the rays and the measuring apparatus was subjected to variation.

The data obtained show that the absorption in oxygen, carbon dioxide, and acetone is proportional to the mass of the molecules, but this relation does not hold for substances containing halogen. The absorption in *iso*butyl chloride, chloroform, carbon tetrachloride, ethyl bromide, and methyl iodide is greater than would correspond with the above relation, and the deviation increases with increasing atomic weight of the halogen. The behaviour of these substances towards high-speed β-rays is therefore quite similar to that which has been already observed in experiments with cathode rays of smaller velocity.

The diffusion measurements show that the diffusion is mainly determined by the mass of the molecules, but deviations are also shown in respect of diffusion by the halogen-containing substances which increase with the atomic weight of the halogen. H. M. D.

The Action of Radium Rays on Mixtures of Hydrogen Arsenide and Oxygen. H. RECKLEBEN and G. LOCKEMANN (*Zeitsch. anorg. Chem.*, 1915, **92**, 145—167).—A mixture of hydrogen arsenide and oxygen is enclosed in a glass vessel with a thin aluminium window over water or salt solution. The temperature and pressure of the gas are read from time to time, the room being darkened. The vessel is a narrow glass cylinder with manometer, the gas capacity being 185 c.c. For some of the experiments the cylinder is divided into short sections by narrow constrictions, each of which bears a mark, to the level of which the liquid may be brought by raising or lowering the reservoir. In the spontaneous reaction of hydrogen arsenide with oxygen, even when the latter is in large excess, the arsenic is liberated in the free state, only the hydrogen being oxidised, but when exposed to β- and γ-rays this reaction is accelerated, and also proceeds further, arsenious acid being formed according to the equation $2H_3As + 3O_2 = 2H_3AsO_3$. α-Rays being excluded, the oxidation cannot be due to the intermediate formation of ozone. C. H. D.

Recent Work on X-Rays and Crystals, and its Bearing on Chemistry. WILLIAM HENRY BRAGG (T., 1916, **109**, 252—269). —A lecture delivered before the Chemical Society.

Radioactivity of Swedish Spring Waters and its Connexion with Geological Formations. NAIMA SAHLBOM (*Arkiv Kem. Min. Geol.*, 1916, **6**, No. 3, 1—51).—In continuation of a previous in-

vestigation (A., 1908, ii, 749), the author has examined the radioactivity of about 400 different spring waters, consisting of deep-bore springs and open drinking-water springs from different geological formations. The difference in the radioactivity between springs from sedimentary formations and those from the primary rocks is very marked, the former having a radioactivity corresponding, on the average, with 4 Mache units, and the latter with 23 Mache units. Of the springs coming from sedimentary rocks, those from chalk have the lowest radioactivity, namely, 1·9 Mache units; then come the shale springs with 2·7 Mache units and the sandstone springs with 7·1 units. The unexpected activity of the latter is confined to the water coming from the Cambrian sandstones, and appears to be caused by the small radium content of the overlying alum shales.

Most of the open springs come from loose glacial deposits, formed chiefly from primary rocks (moraines, etc.), and their activity forms a transition stage to that of the water from the primary rocks. In connexion with the springs from the primary rocks, it is shown that there is a well-marked relation between the radioactivity of the water and the geological character of the rocks; for example, the waters with the highest radioactivities, up to 172 Mache units, come from deep borings in the acid rocks—granites and syenites.

The chemical composition of the rocks through which the water flows has an effect, in that rocks with normal lime and silica content have the greatest radioactivity, whereas a too high content of either lime or silica diminishes the radioactivity. Variations in the radioactivity of waters coming from the same geological formation must be due to variations in the chemical composition of the rocks.

The Swedish spring waters are much more radioactive than other waters, indicating a relatively high radium content of the rocks and mountains. T. S. P.

The Influence of Some Hydroxy-compounds on the Electrical Conductivity of Boric Acid. J. Böeseken, L. W. Hansen, and S. H. Bertram (*Rec. trav. chim.*, 1916, **35**, 309—319. Compare this vol., ii, 73).—With three aromatic hydroxy-ketones examined, namely, benzoyl-, *p*-toluoyl-, and *p*-anisoyl-carbinols, the results obtained show that the action of these substances on boric acid is not important. The actions of pyruvic and lactic acids were compared, and it was found that whilst pyruvic acid, in normal solution, increased the conductivity of boric acid enormously, this high value rapidly diminished with dilution and at a concentration, $N/64$, became slightly negative. Lactic acid in N-solution did not exert quite such a great effect on the conductivity, but the values obtained did not diminish so rapidly with dilution as in the case of pyruvic acid. The authors explain this on the hypothesis that the hydrate of pyruvic acid has five hydroxyl groups, whilst that of lactic acid only has four. The influence of *r*-amygdalic acid on the conductivity of boric acid was also examined, and was found to be only slightly less than that of pyruvic acid in N-solution, but it did not diminish nearly as rapidly with dilution. W. G.

Conductivity. III. Further Studies on the Behaviour of the Alkali Metal Formates in Anhydrous Formic Acid. H. I. Schlesinger and Clyde Coleman (*J. Amer. Chem. Soc.*, 1916, **38**, 271—280).—A continuation of the work of Schlesinger and Martin (A., 1912, ii, 26; 1914, ii, 703). The conductivities, viscosities, and densities of a large number of solutions of different concentrations in formic acid of the formates of lithium, sodium, rubidium, and cæsium have been determined at 18° and 25°. The following conductivity values have been obtained: lithium formate, $K_{25}=0{\cdot}530$, $K_{18}=0{\cdot}515$, $\lambda_{25}=64{\cdot}6$, $\lambda_{18}=56{\cdot}8$; rubidium formate, $K_{25}=1{\cdot}082$, $K_{18}=0{\cdot}989$, $\lambda_{25}=69{\cdot}9$, $\lambda_{18}=61{\cdot}3$; cæsium formate, $K_{25}=1{\cdot}181$, $\lambda_{25}=65{\cdot}0$. The K values are the ionisation constants and the λ values the equivalent conductivities. The following formulæ represent the densities of solutions of the salts in formic acid: sodium formate, $D^{18}=1{\cdot}2233+0{\cdot}0335c$; lithium formate, $D^{25}=1{\cdot}2142+0{\cdot}021c$; $D^{18}=1{\cdot}2224+0{\cdot}0222c$; rubidium formate, $D^{25}=1{\cdot}2142+0{\cdot}085c$; $D^{18}+1{\cdot}2233+0{\cdot}080c$. It is shown that the solutions of these salts in formic acid obey the dilution law when the degree of ionisation is calculated from the conductivity data with correction for viscosity. The value of the ionisation constant increases with the atomic weight of the metal, as also does the conductivity at infinite dilution, cæsium being, however, exceptional. The ionisation constant at 18° is less than that at 25°, which indicates that ionisation in these cases proceeds with absorption of heat. Using these values, the heat of dissociation is calculated to 700, 2180, and 2200 cals. for lithium, sodium, and rubidium formates respectively. J. F. S.

Electrical Conductivity of Acids in Absolute and Aqueous Alcohol. II. Heinrich Goldschmidt [with Max E. Feigl, Carl Görbitz, Haakon Hougen, Kristian Pahle, Jens Schjerve, and Olaf Udby] (*Zeitsch. physikal. Chem.*, 1916, **91**, 46—74. Compare A., 1915, ii, 136).—The electrical conductivity of trichlorobutyric acid, trichloroacetic acid, dichloroacetic acid, salicylic acid, trinitrobenzoic acid, and picric acid, as well as that of the sodium salts of these acids and in many cases the piperidine salts, has been determined at 25° in solutions of absolute alcohol and in alcohol containing measured amounts of water. It is shown that all acids which are slightly dissociated in alcoholic solution are affected in the same way by the addition of water. The change is controlled by the equilibrium constant of the system hydrogen ion–alcohol–water and by the factor $(1+0{\cdot}9n+0{\cdot}3n^2)$ in which n is the normality of the water. The following values were found for the conductivity at infinite dilution for 25°: salicylic acid, 86; dichloroacetic acid, 94; trichlorobutyric acid, 87; trinitrobenzoic acid, 86·5; trichloroacetic acid, 88; and picric acid, 93. The affinity constants for the same acids are $2{\cdot}2\times10^{-9}$, $5{\cdot}2\times10^{-8}$, $1{\cdot}04\times10^{-7}$, $7{\cdot}0\times10^{-7}$, $1{\cdot}5\times10^{-6}$, and $1{\cdot}75\times10^{-4}$ respectively. J. F. S.

Conductivities of Certain Organic Acids in Absolute Ethyl Alcohol. H. H. Lloyd, John B. Wiesel, and Harry C. Jones (*J. Amer. Chem. Soc.*, 1916, **38**, 121—131).—The conductivities of

a large number of organic acids have been determined in absolute alcohol and the molecular conductivities calculated for the temperatures 15°, 25°, and 35°. It is shown that the values are extremely small, being in nearly all cases about several hundred times smaller than in aqueous solution. Dilution increases the molecular conductivity, and in many cases the increase is almost proportional to the volume. The connexion between the conductivity and constitution of the acids is discussed. Malic acid has a conductivity at 15° and $N/32$, which is about thirty times as large as the conductivity of fumaric acid; itaconic acid at 15° and $N/32$ has a value about five times as large as citraconic acid. At 25° and $N/32$ the following molecular conductivities are obtained for the substituted malonic acids: malonic acid, 0·055; ethylmalonic acid, 0·083; diethylmalonic acid, 0·080; propylmalonic acid, 0·105; dipropylmalonic acid, 0·090; butylmalonic acid, 0·036; allylmalonic acid, 0·039; and benzylmalonic acid, 0·062. Phenylpropiolic acid has a molecular conductivity which is about ten times that of cinnamic acid. The conductivities of the para-substituted benzoic acids are generally less than those of the ortho-substituted acids. The strongest acids in alcoholic solution as judged by their conductivity are sulphosalicylic acid and picric acid. The former acid has about the same strength as hydrochloric acid in alcoholic solution. This similarity of strength of the two acids is also found in aqueous solution. J. F. S.

The Conduction of Electricity in Anisotropic Liquids. THEODOR SVEDBERG (*Ann. Physik*, 1916, [iv], **49**, 437—455).—Using *p*-azoxyphenetole and *p*-azoxyanisole as solvents, the author has investigated the influence of temperature on the electrical conductivity of the isotropic and anisotropic solutions which these solvents afford. The results obtained show that the temperature-coefficient for anisotropic solutions is about twice as great as the coefficient for the same solutions in the isotropic condition. At the transition point, the conductivity shows a sharp change. With falling temperature this change amounts to 14% for solutions of hydrogen chloride and to 20—23% for solutions of various organic acids. The magnitude of the change is approximately the same for both the anisotropic solvents examined. H. M. D.

Anodic Relations of Passive Iron with Notes on Polarisation Potentials as Influenced by External Gas Pressures. H. G. BYERS and SETH C. LANGDON (*J. Amer. Chem. Soc.*, 1916, **38**, 362—374).—A number of *E.M.F.* measurements have been carried out with passive iron under various pressures of hydrogen and oxygen respectively. Other experiments have been made on the polarisation potentials of platinum anodes, and copper, iron, and platinum cathodes in $0{\cdot}2N$-sulphuric acid under various pressures of hydrogen and oxygen. The single potentials were measured, using a calomel electrode of special construction, which is described in the paper. On application of gaseous pressures, anodes of passive iron. or any other metallic anode from which oxygen was

being evolved, became more electropositive, and cathodes more electronegative. The change was a function of the mechanical pressure, and not of the degree of saturation of the electrolyte with dissolved gas. Measurements of the variations of polarising current and of anodic potential during the process of passivication gave curves which indicate that passivication was here a two-process operation. It is pointed out that there is no one general explanation of passivity, but rather that in each case the loss of activity is dependent on the conditions. J. F. S.

Convenient Dip Electrode. G. J. van Zoeren (*J. Amer. Chem. Soc.*, 1916, **38**, 652—653).—A dip electrode, which is very rigid in construction, and suitable for determination of the conductivity values and volumetric lead numbers of maple syrups, is described. It consists of two platinum plates, 2 cm.^{2} of 30 gauge. These are fastened by platinum wires to two hard-glass tubes which pass through an ebonite stopper and contain mercury for making the connexions. The platinum plates are 1 cm. apart and are held in this position by four glass rivets, one at each corner. The ebonite stopper, which also carries a thermometer, fits on to a Jena-glass cylinder 3·7 cm. in diameter and 6·5 cm. high, and is clamped in position by two set-screws. The electrode as thus designed is not affected by stirring the very viscous syrups in it, as is the case with all other forms. J. F. S.

The Hydrogen Electrode, the Calomel Electrode, and Contact Potential. W. F. Clarke, C. N. Myers, and S. F. Acree (*J. Physical Chem.*, 1916, **20**, 243—265).—In previous papers, Loomis and Acree (A., 1912, ii, 124 and 125) and Desha and Acree (A., 1912, ii, 125) studied the hydrogen electrode and its application to the determination of hydrogen-ion concentration in organic reactions, etc., whilst Myers and Acree (A., 1914, ii, 164) worked on the improvement of the constancy of the hydrogen electrode and on the standardisation of the calomel cell. In view of its applicability to the study of many questions, such as the hydrolysis of salts, organic and inorganic, the work has been continued, it being desirable eventually to be able to reproduce the potential of the hydrogen electrode accurately to 0·000001 volt.

Attention was first paid to improvements in method and apparatus, including a better form of thermostat, a new type of calomel battery which can be easily and quickly recharged, and a storage reservoir in which hydrogen electrodes can be kept active and constant to 0·0001 volt.

The 0·1*N*-KCl–HgCl–Hg system is constant and reproducible to 0·01 millivolt. The system Hg–HgCl–0·1*N*-KCl–0·1*N*-HCl–Pt–H_2 is a particularly accurate and constant element, whilst the system 0·1*N*-HCl–HgCl–Hg is rather unsatisfactory over long periods of time. Full directions and precautions are given, which must be carefully observed in order to obtain an accuracy and reproducibility of 0·01 millivolt. These relate to purification of materials, regulation of temperature, storage of electrodes when not in use,

and a device for short-circuiting the individual electrodes of a battery to maintain a close agreement. E. H. R.

A Calomel Standard Cell. G. F. LIPSCOMB and G. A. HULETT (*J. Amer. Chem. Soc.*, 1916, **38**, 20—27).—The necessary conditions for the production of a trustworthy standard cell are considered. Based on these considerations, it is shown that a standard cell can be made with calomel instead of mercurous sulphate as depolariser. This cell is built up,

$$CdHg10\% \mid CdCl_2,2\tfrac{1}{2}H_2O(sat.) \mid Hg_2Cl_2 \mid Hg,$$

and is contained in the usual H-shaped vessels. The mercurous chloride is obtained by the electrolysis of a *N*-solution of hydrochloric acid between a mercury anode and a tantalum cathode in a divided cell; the product is grey, due to the presence of finely divided mercury. Tested over many months, this cell is shown to be more constant than either the Clark or Weston cell. It has an *E.M.F.* 0·67080 volt at 25° and a temperature-coefficient $dT/dE = -0{\cdot}000067$ volt. The heat change of the reaction $Hg_2 + CdCl_2 = Hg_2Cl_2 + Cd$, which occurs in the cell, is calculated from the above data by means of the Gibbs-Helmholtz equation and found to be 30060 cal. This value agrees well with the value 30036 cal. found from thermochemical data. Measurements have also been made with cells containing non-saturated solutions of cadmium chloride. With a solution containing 52 grams of cadmium chloride in 100 grams of solution, an *E.M.F.* 0·68120 volt was found at 25° with a temperature-coefficient 0·000285. Other values are given in the paper which show that the temperature-coefficient does not change much with the concentration of the solution. J. F. S.

Inclusions in Silver Voltameter Deposits. G. W. VINAL and WM. M. BOVARD (*J. Amer. Chem. Soc.*, 1916, **38**, 496—515).—The mechanically held inclusions in the deposits of silver in silver voltameters have been made the subject of a searching investigation. Silver deposits have been heated at temperatures slightly above 600° both in the Bunsen flame and in an electric furnace. The losses in weight indicate the presence of foreign material in the deposits to the extent of 0·0040% on the average for pure electrolytes and higher values for impure electrolytes. It is found that such heating of the deposits produces an alloy of silver and platinum, which, when the silver is dissolved, leaves a thin film of platinum-black that may lead to serious errors the next time the cup is used if proper precautions are not taken. As the result of the work, it is shown that the most accurate value for the electrochemical equivalent of silver is 1·11800 mg. per coulomb, and therefore the value of the Faraday becomes 96494 absolute coulombs, but for general purposes 96500 as a round number is to be recommended. Inclusions in silver deposits made on smooth platinum surfaces are the same to within the experimental error as when the deposits are made on matte surfaces. Inclusions between the crystals and cup have been measured by an application

of the conductivity method, and found to be a negligible part of the total inclusions, which with pure solutions were about 4 parts per 100,000. In cases where the deposit in large cups exceeds that in small cups, that is, where the volume effect is appreciable, it is not found that strong heating of the deposits diminishes the difference. Two experiments on the anode liquid support the conclusion of the American Bureau of Standards that a heavy anode ion is non-existent. J. F. S.

Factors Affecting the Electromotive Force of Binary Solid Alloys. DONALD P. SMITH and NEWELL T. GORDON (*J. Physical Chem.*, 1916, **20**, 228—242).—In studying the physical properties of alloys, the greatest difficulty encountered is the preparation of samples of uniform composition and structure. Particular care was taken in the preparation of samples of brass to eliminate traces of oxide, and to obtain uniformity of structure by preparing surfaces from horizontal layers of the solidified mass by long annealing of the specimens in a vacuum at 700—750°. The factors most in need of investigation, affecting the *E.M.F.* of a binary alloy against an electrolyte, are the effect of heat and surface treatment and the composition of the electrolyte. In order to test the theory developed by Nernst and Reinders, a method is needed for ascertaining the composition of the equilibrium electrolyte.

In one set of experiments described, the *E.M.F.*, with reference to the electrode $Hg/Hg_2SO_4,2NH_2SO_4$, of a brass containing 49·9% of copper was measured, using electrolytes 1.10^{-5} to 1.10^{-6} normal in copper and normal in zinc and sodium sulphates. So long as the surface was untreated between the experiments, the *E.M.F.* was reproducible to within a few millivolts, a steady "drift" with change in composition of the electrolyte being observed in every case. For instance, with the electrolyte 1.10^{-5} normal in copper, the *E.M.F.* fell from 0·480 to 0·470 volt in one hundred and fifty minutes. The necessity for employing the equilibrium electrolyte is emphasised.

Surface treatment of the specimen, between experiments, with rouge or emery, was found to produce marked and inexplicable variations in *E.M.F.* The influence of sawing, grinding, and polishing on the potential must be first investigated. E. H. R.

Law of Thermal Expansion of Liquids Below the Normal Boiling Point. ALFRED ALBERTOSI (*J. Chim. phys.*, 1915, **13**, 390—398).—By combining Dupré's empirical formula for the change of the vapour pressure of a liquid with temperature, $\log p = m/T + n \log T + z$, in which m, n, and z are constants, with Clausius's thermodynamic formula, the relation $p(n/T - m/T^2) = L/T(v' - v)$ is obtained, in which L is the latent heat of vaporisation, v' and v the specific volumes of saturated vapour and liquid respectively. By substituting for L the value given in an earlier paper (this vol., ii, 218), and assuming that the saturated vapour satisfies the simple gas laws, the above equation gives

$d^{5/3}=RT(n-1)/a-Rm/a$, which may be written in the form $d^{5/3}=A-BT$, where A and B are constants.

Comparison of the experimental data for the expansion of a number of liquids shows that the results are in remarkably good agreement with those calculated with the aid of this formula. It may be noticed that the constant A represents the density of the liquid at absolute zero, and that the formula may be applied in the calculation of such limiting densities. H. M. D.

Simultaneous Action of Very High Pressures and Temperatures on Chemical Phenomena. Cosmogonical Applications: Chemical Origin of Solar Radiation; Discussion of Arrhenius's Theory. E. BRINER (*J. Chim. phys.*, 1915, **13**, 465—487).—A consideration of the influence of very high pressures on high temperature systems, which at moderate pressures would consist almost entirely of elementary atoms, shows that the temperature effect would in a large measure be counterbalanced by the pressure effect, and that simple and compound molecules should be capable of existence under these conditions.

The formulæ expressing the relation between the pressure, temperature, and degree of dissociation are applied to the dissociation of hydrogen, ammonia, and nitric oxide, and the influence of pressure at high temperatures is derived in each case.

Arrhenius's theory, according to which the energy of solar radiation is attributable to the decomposition of endothermic compounds, is adversely criticised. The possibility that this energy has its origin in the combination of elementary atoms to form molecules is also examined, but it would seem that the energy which would thus become available is far too small to account for the sun's radiant energy. To account for this, it would seem necessary to assume that the entities involved in the process of molecular synthesis are of sub-atomic character. H. M. D.

Equation of State for Gases and Liquids. F. H. MACDOUGALL (*J. Amer. Chem. Soc.*, 1916, **38**, 528—555).—A mathematical paper, in which the Dieterici equation, $p=RT/(v-b)\,.\,e^{-a/vRT}$, is discussed in detail, and the extent to which this equation reproduces the experimental facts is shown in several ways. A number of methods are developed for calculating the values of a and b, below, at, and above the critical temperature. A formula is deduced for calculating the pressure of saturated vapour from the densities of liquid and vapour. This equation has the form $p_s=(d_1+d_2)RT\,.\,e^{-a(d_1+d_2)/2RT}$, in which d_1 and d_2 are the densities of the liquid and saturated vapour respectively. A formula is deduced for calculating the latent heat of vaporisation from the densities of the liquid and saturated vapour. This formula has the form $L=2RT\log_e v_2/v_1=a/v_1-a/v_2$. The previously observed values of *iso*pentane, carbon dioxide, and hydrogen are studied in connexion with these formulæ. In the case of *iso*pentane, a decreases and b increases from 0° up to the critical temperature. The same is true of carbon dioxide. Above the critical temperature, in

the case of carbon dioxide, *a* continues to decrease, whilst *b* remains fairly constant up to 200°. In the case of hydrogen, *a* decreases from the critical temperature up to the ordinary temperature, whilst *b* does the same from −183° at least. The inversion temperature is calculated in the case of hydrogen and also the temperature at which it is in accord with Boyle's law for moderate pressures. The latter temperature was found to be −171·4°. On combining the law of Cailletet and Mathias with a result obtained in many cases by Young, it is shown that the density of a substance at the absolute zero is four times the critical density. The author's conclusions in regard to the variations of *b* with temperature are in accord with some of the views of Richards in connexion with the compressibility of atoms. J. F. S.

Consideration of the Critical Opalescence. ETTORE CARDOSO (*J. Chim. phys.*, 1915, **13**, 414—425. Compare A., 1913, ii, 109, 110, 111).—The opalescence exhibited by carbon dioxide and other substances in the neighbourhood of the critical temperature has been found, in agreement with previous observations, to vary in character with the filling of the tube containing the substance. This variation shows itself in the temperature at which the opalescence is a maximum and also in the length of the interval in which the opalescence is visible. The phenomenon has not been observed in the author's experiments with oxygen, nitrogen, carbon monoxide, and methane, and it is suggested that this may be due to the shortness of the opalescent interval in the case of gases of low critical temperature.

An examination of the hypothesis that the opalescence is due to the formation of an emulsion leads to the conclusion that this offers no satisfactory explanation of the facts. On the other hand, it is claimed that the apparent absence of the phenomenon in gases of low critical temperature is in accord with Smoluchowski's view that the heterogeneity which gives rise to the opalescence is connected with the velocity distribution of the molecules. An analysis of Maxwell's formula indicates that the velocities of the molecules will tend towards a uniform value as the temperature falls, and local differences in density will consequently become less marked.
H. M. D.

Variations of the Specific Heats of Gases with the Pressure. THADÉE PECZALSKI (*Ann. Physique*, 1916, [ix], **5**, 113—120. Compare A., 1914, ii, 527).—A mathematical discussion of the subject.
W. G.

Determination of the Velocity of Sound and of the Ratio of the Specific Heats of Gases by Kundt's Dust Figure Method. GUSTAV SCHWEIKERT (*Ann. Physik*, 1916, [iv], **49**, 433—436. Compare this vol., ii, 79).—An addendum to the previous paper, giving a summary of recent determinations of the specific heat ratio and of the specific heat at constant pressure. H. M. D.

The Ratio of the Specific Heats $K = c_p/c_v$ of Nitrogen. F. A. SCHULZE and H. RATHJEN (*Ann. Physik*, 1916, [iv], **49**, 457—469). —The specific heat ratio has been determined for carefully purified nitrogen by Kundt's method, giving $c_p/c_v = 1{\cdot}4144 \pm 0{\cdot}0002$ at room temperature and a pressure of 1 atmosphere. This value leads to $4{\cdot}193 \times 10^7$ erg for the mechanical equivalent of the calorie. Recent measurements of the specific heat ratio for air, oxygen, and hydrogen afford for the mechanical equivalent 4·209, 4·188, and $4{\cdot}202 \times 10^7$ erg respectively. The agreement between these several values is much closer than that indicated by older measurements.

H. M. D.

The Latent Heat of Fusion of Ice. A. LEDUC (*Ann. Physique*, 1916, [ix], **5**, 5—17).—A report presented to the third International Congress of Cold (Washington-Chicago, September, 1915), in which the work on this subject is summarised and the value 79·6 cal. deduced for the latent heat of fusion of ice at 15°. W. G.

Cryoscopic Measurements at Low Temperatures. H. S. REID and D. MCINTOSH (*J. Amer. Chem. Soc.*, 1916, **38**, 615—625). —The molecular weights of a number of oxygen-containing organic liquids of low melting point have been determined in solution in hydrogen bromide by the cryoscopic method. The liquids examined were: ethyl alcohol, methyl alcohol, ethyl acetate, ethyl ether, acetone, acetic acid, paracetaldehyde, and acetaldehyde. Experiments were also made with bromine. The cryoscopic constant for hydrogen bromide was found to be 103·1 from experiments on toluene, chloroform, and carbon tetrachloride. The results show that all the compounds which form compounds with hydrogen bromide are both associated and dissociated, the amount of association varying very much with the substance. The amount of association agrees fairly well with the figures obtained for the molecular conductivity, the substances showing the greatest amount of association having the greatest conductivity. A comparison of the properties of ethyl ether and ethyl alcohol in hydrogen bromide is made with similar solutions in chlorine. Oxonium compounds are formed in both cases, and a study of the slopes of the freezing curves shows that in solution these compounds are largely broken down into their constituents. Solutions in chlorine are non-conductors, that is, they exhibit no electrolytic dissociation. The determinations of molecular weights in liquid chlorine made recently by Waentig (A., 1910, ii, 581) show normal results for ethyl ether over a considerable concentration, whilst methyl alcohol and ethyl alcohol are greatly polymerised. There are, therefore, systems in which the compounds are broken down partly into their constituents which are further complicated by association and in some cases by electrolytic dissociation. Hence it is at present impossible to assign to these three factors their proper proportion and to give formulæ to oxonium compounds. The increase in complexity in solution shown by the increasing values of the molecular weights points to the correctness of the view previously expressed that the

ions are much more complex than would be expected from the oxonium theory. J. F. S.

Mathematical Relationship between the Boiling Point and Absorption Coefficient of Gases. A. Imhof (*Zeitsch. physikal Chem.*, 1916, **91**, 124—128).—A theoretical paper, in which the connexion between the boiling point and the absorption-coefficient of gases is studied. It is shown that for the majority of the gases which obey Henry's law, the boiling point is approximately proportional to the logarithm of the absorption-coefficient at 0° and 760 mm. for water, if $-100°$ is taken as the zero of temperature. On the other hand, if the temperatures are measured in absolute degrees, the boiling points of various gases bear the same relationship to one another as do the logarithms of their absorption-coefficients: $T_1 = \lambda \log a_1$; $T_2 = \lambda \log a_2$ or $T_1/T_2 = \log a_1/\log a_2$. The value of the constant has been determined and found to be 27·4, so that $T = 27{\cdot}4 \log_e . a$ or $a = e^{T/27{\cdot}4}$. J. F. S.

Formula for the Calculation of the Heat of Vaporisation of Non-associated Liquids. Alfred Albertosi (*J. Chim. phys.*, 1915, **13**, 379—389).—On the assumption that the attraction between two spherical molecules varies directly as the product of the masses and inversely as the sixth power of the distance between them, the author has derived the formula $L = \alpha(d^{5/3} - d'^{5/3}) - \beta d'(1 - d'/d) + p(v' - v)$ for the latent heat of vaporisation L. In this, α and β are constants, v and v' the specific volumes of liquid and saturated vapour respectively at pressure p, and d and d' are the corresponding densities. At low temperatures d' is very small and the formula reduces to $L - p(v' - v)/(d^{5/3}d'^{5/3}) = \alpha$.

It is shown by reference to the data for a number of organic liquids that the heats of vaporisation calculated by means of this formula over a considerable temperature range are in good agreement with those derived thermodynamically from Young's data for the vapour pressures. The deviations are of the order of 0·2—0·5%. H. M. D.

Vapour Pressure of Solutions. Lowering of the Vapour Pressure of Water Produced by Dissolved Potassium Chloride. B. F. Lovelace, J. C. W. Frazer, and E. Miller (*J. Amer. Chem. Soc.*, 1916, **38**, 515—528).—The authors have previously (A., 1915, ii, 11) described an apparatus for the determination of the vapour pressure of solutions. This apparatus has now been improved by a more sensitive temperature regulation, which makes it possible to keep the temperature constant to within 0·01° for twelve hours, by the introduction of a mechanical device for stirring the solutions under investigation during the experiment and by the addition of a more sensitive McLeod gauge for measuring the residual air pressure after the absorption of the water-vapour. The actual observations of the vapour pressure were only made after the McLeod gauge had shown a residual air pressure of less than 0·0001 mm. Under these conditions the vapour pressure of a given

solution remains constant for days to 0·001 mm. A number of solutions of potassium chloride of concentration 0·2—2·0N have been investigated with regard to their vapour pressure by the above-mentioned apparatus. It has been shown by analysis of the solutions from the apparatus, after the measurements have been made, that the change of concentration of the solutions during the process of removing the dissolved air and measuring the vapour-pressure lowerings is small enough to be neglected. The most notable feature of the experimental results is that the molecular lowering is the same for all solutions investigated. Thus a 0·2N-solution gives a lowering of 0·110 mm., whilst a 2N-solution gives a lowering of 1·1102 mm. Similar results have been obtained by Tower and Germann (A., 1915, ii, 11) from the vapour tension of alcoholic solutions of potassium bromide and lithium chloride. The authors are unable to decide whether this phenomenon, as suggested by Tower and Germann, is due to the combination of solvent and dissolved substance or not. J. F. S.

The Relation between Surface Tension and Other Quantities. MASAO KATAYAMA (*Sci. Rep. Tohoku Imp. Univ.*, 1916, **4**, 373—391).—The surface tension at the surface of a liquid in contact with its saturated vapour is influenced by the vapour as well as by the liquid. An attempt is made to eliminate the effect of the vapour by subtracting the number of molecules in unit volume of the vapour from the number in unit volume of the liquid. The molecular volume of the fictitious liquid resulting thereby is given by the equation $V' = M/D_l - D_v$, in which D_l and D_v are the orthobaric densities of liquid and vapour respectively, and M is the molecular weight of the substance. The molecular surface energy, measured by $\gamma V'^{\frac{2}{3}}$, is then found to be a linear function of the temperature until the critical temperature is nearly reached. This is shown by reference to the data for benzene, chlorobenzene, carbon tetrachloride, ethyl ether, ethyl acetate, and methyl formate.

From van der Waals's equation connecting the surface tension and temperature and the Eötvös equation, the author deduces the relation $D_l - D_v = 3{\cdot}03(1-\theta)^{0{\cdot}351}D_k$ between the orthobaric densities D_l and D_v at the reduced temperature θ and the critical density D_k.

A further relation is that connecting the total surface energy u and the free surface energy γ, which has the form

$$u/\gamma = (1 + 0{\cdot}234\theta)/(1-\theta),$$

and this is found to be in good agreement with experiment. H. M. D.

Changes in Volume on Solution in Water of the Halogen Salts of the Alkali Metals. II. GREGORY PAUL BAXTER and CURTIS CLAYTON WALLACE (*J. Amer. Chem. Soc.*, 1916, **38**, 70—105. Compare A., 1911, ii, 557).—The densities of aqueous solutions of the chlorides, bromides, and iodides of the metals lithium, sodium, potassium, rubidium, and cæsium have been determined for a large number of concentrations from saturation down-

wards at temperatures of 100°, 70·19°, 50·04°, 25°, and 0°. From the density values the change in volume is calculated, and also the change in volume per gram of dissolved salt and per gram-molecule of salt. Voluminous tables of results are given, which include the whole of the experimental data and the calculated quantities. The changes in volume observed can be explained by Richard's hypothesis of compressible atoms and that of hydration. This explanation assumes that the following two changes, which take place during solution and dissociation, are the chief causes of the observed effects: (i) When the molecules dissociate, they are, to a large extent, freed from compression due to chemical affinity, and in consequence there is a large expansion amounting to 15—56% of the volume of the uncombined elements; (ii) when the ions, and probably the molecules, are combined with water, both the hydrated substance and the water undergo compression. The latter effect varies regularly with the compressibilities of the substances involved as well as with their affinities for each other. The change in volume in the formation of the solution from the free halogens and the alkali metals and water is found to be nearly additive at all concentrations; at low concentrations because the changes involved are chiefly due to the formation of ions from the elements, which are independent of the salts involved; at high concentrations because the molecules, being less hydrated and less compressible, produce smaller contractions, and because the molecular volumes of the salts are very nearly additive. The effect of rising temperature is found in general to diminish contraction or increase expansion owing to lessened hydration of all the substances concerned. Marked exceptions exist at the ordinary temperature in lithium chloride and bromide, and also in the case of potassium bromide at high temperatures. It is pointed out that no simple method exists for separating the effects due to ionised and non-ionised material because of the varying magnitude of the change for each ion or molecule with changing concentration. J. F. S.

Densities and Cubical Coefficients of Expansion of the Halogen Salts of Sodium, Potassium, Rubidium and Cæsium. Gregory Paul Baxter and Curtis Clayton Wallace (*J. Amer. Chem. Soc.*, 1916, **38**, 259—266. Compare preceding abstract). The values of the densities of the above-mentioned salts were required at various temperatures in the calculations connected with the work described in the previous paper. The densities and coefficients of cubical expansion were deduced from results obtained by weighing known quantities of the material in toluene, and by measuring the volume of toluene displaced by known weights of the materials at various temperatures. The following densities were found: sodium chloride, 70·19°, 2·153; 50·04°, 2·156; 25°, 2·161; 0·00°, 2·168; sodium bromide, 50·04°, 3·194; 25·0°, 3·203; 0°, 3·213; sodium iodide, 50·04°, 3·653; 25°, 3·665; 0°, 3·677; potassium chloride, 70·19°, 1·978; 50·04°, 1·981; 25°, 1·987; 0°, 1·992; potassium bromide, 50·04°, 2·740; 25°, 2·749; 0°, 2·756; potassium iodide, 50·04°, 3·114; 25°, 3·123; 0°, 3·133; rubidium chloride, 50·04°,

2·792; 25°, 2·798; 0°, 2·806; rubidium bromide, 50·04°, 3·340; 25°, 3·349; 0°, 3·358; rubidium iodide, 50·04°, 3·542; 25°, 3·550; 0°, 3·560; cæsium chloride, 70·19°, 3·952; 50·04°, 3·961; 25°, 3·974; 0°, 3·988; cæsium bromide, 50·04°, 4·418; 25°, 4·433; 0°, 4·449; cæsium iodide, 50·04°, 4·493; 25°, 4·509; 0°, 4·525. A list of values found by other observers is included in the paper.

J. F. S.

Densities and Cubical Coefficients of Expansion of Certain Substances: As_2O_3, $PbCl_2$, $PbBr_2$, $PrCl_3$. GREGORY PAUL BAXTER and CHARLES FRANCIS HAWKINS (*J. Amer. Chem. Soc.*, 1916, **38**, 266—271).—The densities of the above-named substances have been determined by weighing in a toluene-filled pyknometer at 50°, 25°, and 0°. The following values were obtained: arsenious oxide (octahedral), 50°, 3·851; 25°, 3·865; 0°, 3·874; lead chloride, 50°, 5·872; 25°, 5·885; 0°, 5·899; lead bromide, 50°, 6·644; 25°, 6·669; 0°, 6·676; praseodymium chloride, 25°, 4·020. The coefficients of cubical expansion of the first three substances have been calculated. A list of previous determinations of these quantities by other observers is included in the paper. J. F. S.

Van der Waals's Equation. W. V. METCALF (*J. Physical Chem.*, 1916, **20**, 177—187. Compare this vol., ii, 85).—By rearrangement of its terms, van der Waals's equation becomes an expression of equilibrium between opposing pressures, $P_1+P_2=P_3$. Here $P_2(=a/v^2)$ is the cohesive pressure due to the attraction between the molecules, and $P_3(=RT/v-b)$ is the elastic pressure tending to increase the volume of the mass, P_1 being the external pressure. Certain conclusions were reached in the previous paper connecting important points on the volume–temperature curves with the rate of change with volume (or density) of these opposing pressures, and in the present paper these conclusions are confirmed by a rigid mathematical analysis of the equation. E. H. R.

Sources of Error in Viscosity Measurement. EUGENE C. BINGHAM, H. I. SCHLESINGER, and ARTHUR B. COLEMAN (*J. Amer. Chem. Soc.*, 1916, **38**, 27—41).—Whilst working with the Bingham viscosimeter (A., 1914, ii, 342) the authors found that the viscosities, when calculated by the generally accepted formula, were not constant, but varied with the pressure applied. They were thus led to investigate the various points in the construction, method of use, and interpretation of various factors, of viscosimeters. It is shown that the average pressure to be used in the calculation of a viscosity measurement is not strictly one-half the sum of the initial and final pressures, as ordinarily assumed, and the use of this value may lead to considerable error. The method of arriving at the true average pressure has been deduced and tested experimentally. In the flow of a liquid through a capillary tube it is immaterial, for purposes of viscosity measurement, whether the capillary is horizontal or vertical. When a liquid flows from a capillary with a trumpet-shaped opening there is a

definite loss of kinetic energy, but whether the correction for this is the same as that in the case of a capillary with a uniform bore has not been proved. As a result of the work, it is suggested that the capillaries of viscosimeters should have ends which are as nearly square as possible, so that the kinetic energy correction may be readily calculable, also that the bulbs should be as short as possible. The latter is achieved by making each bulb approximately of the shape of two cones placed base to base. J. F. S.

Change of the Internal Friction of Metals with Temperature. P. LUDWIK (*Zeitsch. physikal. Chem.*, 1916, **91**, 232—247).—With the object of investigating the change of internal friction with temperature, the hardness of the metals tin, bismuth, cadmium, lead, zinc, antimony, aluminium, and copper has been determined at temperatures from 20° to the melting point in most cases, and in those cases where the metal melts above 600° the measurements have been carried out up to that temperature. The method employed was the cone pressure method, the pressure applied varying from 5 to 1000 kilograms for fifteen and three hundred seconds. From curves of the experimental results it is shown that the decrease of the hardness and internal friction with increase of temperature is fairly steady. Irregularities, due to changes in the modification of the metal, do not seem to be important. A comparison of the hardness figures at similar and at homologous temperatures shows that the change in hardness is not the same for various metals, since the curves repeatedly cross one another; consequently the hardness is to be regarded as dependent on the temperature at which it is determined. At the melting point the hardness still possesses a considerable value; thus for tin and bismuth it has 10% of its original value; cadmium, 2%; lead, 7%; zinc, $1\frac{1}{2}$%. A sudden fall in the hardness only occurs as the metal melts. The internal friction of a solid metal therefore passes, as the metal melts, suddenly into the viscosity of the molten metal.
J. F. S.

Surface Tension I. Drop Weight Method for the Determination of Surface Tension. WILLIAM D. HARKINS and E. C. HUMPHERY (*J. Amer. Chem. Soc.*, 1916, **38**, 228—236).—The drop method offers the most exact means of determination of surface tension, but owing to faulty theoretical treatment of experimental data widely divergent results are obtained. The ideal conditions are represented by the equation $W=2\pi r\alpha$, where W is the weight of the drop, r the radius of the tip of the dropping tube, and α the surface tension. This equation is only true if the pendant drop is entirely supported by the surface tension and if the whole of the drop falls. Neither condition obtains in practice. The subject was treated theoretically by Lohnstein (A., 1909, ii, 25), who evolved the formula $W=2\pi r\alpha f(r/a)$, in which a is the square root of the capillary constant. The function $f(r/a)$ therefore represents a correcting factor, which was calculated by Lohnstein for various values of r/a. These the authors find are not sufficiently accurate

if values of the surface tension more accurate than 4% are required. They have therefore determined experimentally the values of $f(r/a)$, using a two-liquid interface at temperatures of 10°, 20°, 25°, and 30°. The receiving liquids were benzene, ethyl carbonate, dimethylaniline, xylene, toluene, hexane, whilst the dropping liquid was water, benzene, or solutions of sodium chloride or strontium bromide. Some experiments were carried out by allowing the drop to fall into air. The experimental values are compared with the theoretical values of Lohnstein; the former give a very much smoother curve than the latter. J. F. S.

Surface Tension. II. Apparatus for the Determination of the Surface Tension at the Interface between Two Liquids. WILLIAM D. HARKINS and E. C. HUMPHERY (*J. Amer. Chem. Soc.*, 1916, **38**, 236—242. Compare preceding abtsract).—A description of apparatus for determining surface tension by both the drop method and the capillary rise method is given in the paper. The apparatus in the former case consists of a pipette of about 10 c.c. capacity graduated in 1/10 c.c. above and below the bulb. Below the lower graduations a capillary tube of 0·3 mm. diameter is attached; this is bent upward, and at the height of the bulb bent downward again. The end of the capillary tube passes through a stopper in a small vessel designed to hold the second liquid. The dropping end of the tube was 9·4 mm. diameter, since it was found that with this dimension the value of the correcting factor, $f(r/a)$, is most accurately known. A second tube, attached to a suction apparatus, also passes through the stopper of the containing vessel. The method of effecting a determination consists in filling the pipette to slightly above the zero graduation and then just bringing the level to the zero mark. The end is then placed in the second liquid and the temperature of the whole allowed to become constant. The exhausting pump or tube is then so arranged that a drop of liquid will form and fall in three to three and a-half minutes. When this has happened, the volume of the drop is read off from the pipette and the weight calculated. A piece of apparatus is described for measuring the surface tension at the interface of two liquids by the capillary rise method. For the actual details the original paper must be consulted. A very novel feature is the method of producing capillary tubes of uniform bore. The tubes are of Jena glass and of about 1·4 mm. diameter, uniformity being obtained by turning the bore in an accurate and sensitive lathe.
J. F. S.

Surface Tension. III. Surface Tension at the Interface between Two Liquids and the Effect of Acids, Salts, and Bases on the Interfacial Tension. WILLIAM D. HARKINS and E. C. HUMPHERY (*J. Amer. Chem. Soc.*, 1916, **38**, 242—246. Compare preceding abstracts).—The surface tension at the interface between water and benzene has been determined at 10°, 20°, 25°, 30°, and 40° by the capillary rise method. The value of the surface tension at any temperature is given by the formula $\alpha = 35{\cdot}54(1 - 0{\cdot}056t)$. The

surface tension at the interface between water and ethyl carbonate, dimethylaniline, xylene, toluene, and hexane has been determined at 25° by the same method. The values found are about 6% higher than those previously obtained by von Lerch (A., 1913, ii, 13) and Antonoff (A., 1907, ii, 606). The effect of acids, bases, and salts on the surface tension at the benzene–water interface has been studied. It is shown that inorganic acids (HCl, H_2SO_4), bases ($NH_4 \cdot OH$), and salts (NaCl) lower the surface tension only very slightly, but organic acids (formic, acetic, and butyric) produce a marked lowering, the value being greater the higher the molecular weight of the acid. The following figures for approximately $N/2$-solutions of the acid show the effect: pure water, 34·18; $N/2$-formic acid, 32·49; $N/2$-acetic acid, 29·24; and $N/2$-butyric acid, 22·45. These results are particularly interesting in connexion with muscular action. J. F. S.

Simple Apparatus for the Accurate and Easy Determination of Surface Tension, with a Metal Thermoregulator for the Quick Adjustment of Temperature. WILLIAM D. HARKINS and F. E. BROWN (*J. Amer. Chem. Soc.*, 1916, **38**, 246—252).—An apparatus is described for the determination of surface tension by the drop-weight method. It consists essentially of two weighing bottles fitted with glass or monel-metal stoppers. One of these bottles contains the liquid under investigation, and the other receives the drops. The two bottles are connected by a capillary U-tube with a long and a short limb; the end of the short limb furnishes the dropping surface. The dropping tip is so ground that interchangeable tips of monel-metal can be attached, thus enabling a rapid change of the diameter to be made. Into each stopper a capillary tube enters, just passing through the stopper, the one to produce a slightly reduced pressure in the dropping bottle and the other to admit air to the reservoir. A mercury burette is described for the production of the suction. Both weighing bottles and their connexions are placed in a nickel-plated brass box with glass sides, which enables the whole apparatus to be sunk in a thermostat. Complete working details for making the apparatus are given in the paper. J. F. S.

Properties of Mixed Liquids. I. Sulphuric Acid–Water Mixtures. J LIVINGSTON R. MORGAN and CLARKE EDWIN DAVIS (*J. Amer. Chem. Soc.*, 1916, **38**, 555—568).—A large number of surface-tension measurements have been made by the drop-weight method, with solutions of sulphuric acid of concentrations from that of pure water to pure sulphuric acid at temperatures 0°, 30°, and 50°. Formulæ have been deduced by means of which the surface tension and specific cohesion can be calculated at any concentration and temperature between 0° and 50°. In the case of the more concentrated solutions, difficulties were encountered in the formation of the drop owing to the poor way in which it covered the tip. This was got over by rapidly forcing out the drop and then withdrawing it several times until the tip was properly

covered and then allowing it to form in the normal manner. It is shown that both the addition of sulphuric acid to water and of water to sulphuric acid cause an increase in the surface tension, so that different concentrations of sulphuric acid may have the same surface tension at the same temperature. The addition of sulphuric anhydride to sulphuric acid also increases the surface tension. If the property–composition curve has any chemical meaning it may be assumed from the surface tension results that a hydrate, H_2SO_4,H_2O, exists at 85% sulphuric acid. The application of the theory of Denison (A., 1913, ii, 30), that the deviation of a property from the mixture lay plotted against the composition shows at the point of maximum deviation the presence of a compound of identical composition with that of the solution leading to the maximum deviation, indicates the following hydrates in water solutions of sulphuric acid according to the property which is taken as the criterion: H_2SO_4,H_2O (density, compressibility, viscosity, refraction), $H_2SO_4,2H_2O$ (refraction), $H_2SO_4,3H_2O$ (surface tension), $3H_2SO_4,H_2O$ (conductivity, viscosity), $H_2SO_4,12H_2O$ (conductivity, density), $4H_2SO_4,H_2O$ or $5H_2SO_4,H_2O$ (viscosity). J. F. S.

Adsorption. V. GERHARD C. SCHMIDT and BERNHARD HINTELER (*Zeitsch. physikal. Chem.*, 1916, **91**, 103—123. Compare A., 1912, ii, 236; 1913, ii, 677).—The adsorption of vapours of benzene, hexane, carbon disulphide, chloroform, acetone, ethyl alcohol, methyl alcohol, and water by bone charcoal has been determined up to the saturation point at 14·2°. It is shown that for those liquids which are normal the saturation value is approximately proportional to the molecular volume of the liquid. For associated liquids no proportionality exists, in some cases the product of the saturation value and the molecular volume being larger than in the case of normal liquids and in some cases smaller. The exponential formulæ, $c_1=kc_2^{\alpha}$ and $c_1=\pi(c_2/S)^{\alpha}$, express the experimental results up to saturation fairly accurately. In these expressions c_1 is the concentration of the vapour, c_2 the quantity adsorbed, π the vapour tension, S the saturation value, and k and α constants. Schmidt's formula (*loc. cit.*), $(a-x)/v \,.\, S=Ke^{A(S-x)/S} \,.\, x$, where $(a-x)/v$ is the concentration, S the saturation value, x the adsorbed quantity, and K and A constants, expresses the experimental results for benzene, but fails entirely in all other cases. Consequently, this formula is not to be used further as the adsorption isothermal. J. F. S.

Geochemical Metal Adsorption. OSKAR NAGEL (*Kolloid. Zeitsch*, 1915, **16**, 19—20).—Reference is made to the natural occurrence of platinum, gold, silver, and vanadium in deposits which seem to show that the metals have been adsorbed by the matrix. In this connexion the author calls attention to the large adsorption of clays in respect of potassium compounds. H. M. D.

Simultaneous Adsorption by Two Adsorbing Media. HILARY LACHS (*Zeitsch. physikal. Chem.*, 1916, **91**, 155—170).—A number

of adsorption experiments have been carried out at room temperature, using simultaneously two of the following adsorbents: charcoal, wood, alumina, meerschaum, and quartz. Solutions of acetic acid, butyric acid, succinic acid, sodium hydroxide, pyridine, and acetone were shaken with known quantities of each of the adsorbents separately and with a mixture of two of the adsorbents, and the equilibrium conditions determined. The object of the investigation was to ascertain the equilibrium conditions in the presence of two adsorbents and to ascertain whether two oppositely charged adsorbents effected a change in the amount of adsorption of either or both of the individual adsorbents. It is shown that if the solutions are not too dilute, irrespective of the nature of the adsorbents, the quantity of material adsorbed by a mixture of adsorbents is the sum of the quantities adsorbed by the adsorbents separately. If the solutions are very dilute the amount adsorbed by a mixture is less than the sum of the amounts adsorbed by the adsorbents separately. In the case of solutions of acids and bases, and to some extent in the case of acetone, the equilibrium constant is the same, whether the adsorbents are mixed or are kept in separate compartments. In the case of colour substances (methylene-blue, crystal-violet, new magenta, and auramine), the equilibrium constant is different in the two cases. J. F. S.

The Adsorption of Acids by Cellulose. ALAN LEIGHTON (*J. Physical Chem.*, 1916, **20**, 188—194. Compare this vol., ii, 128).—The behaviour of sulphuric, phosphoric, or hydrochloric acid of varying concentration towards cellulose in the form of surgeons' cotton purified by treatment with 1% sodium hydroxide, was studied by shaking about 1 gram of cellulose with 100 c.c. of acid for three hours and then centrifuging for one hour. The acid retained by the cotton was estimated gravimetrically, and the centrifuged acid was titrated to determine if any change in concentration had taken place through selective adsorption. Curves were plotted illustrating the increase in adsorption with increasing concentration of each acid. Selective adsorption is shown only at high concentration, and is most marked in the case of hydrochloric acid; with sulphuric acid it begins at a concentration of 400 grams per litre; it is not detected with phosphoric acid. The value of the adsorption, expressed in grams, is greatest with sulphuric and least with hydrochloric acid. No evidence of the formation of a compound between acid and cellulose was discovered. The presence of acid lowers appreciably the amount of water adsorbed by the cotton. E. H. R.

The Adsorption of Dyes by Colloidal Clay, etc. PAUL ROHLAND (*Kolloid. Zeitsch.*, 1915, **16**, 16—18).—In general, the adsorption of dyes by colloidal silicates increases with increase in the colloidal nature of the dye. The constitution of the dye also seems to have an influence on the phenomenon. Dyes derived from triphenylmethane are in general readily adsorbed, whilst those containing nitro- or azo-groups are adsorbed with greater difficulty.

The differences exhibited by colloidal silicates towards dyes may be utilised in separating dyes from their mixtures. H. M. D.

Abnormal Osmosis. H. FREUNDLICH (*Kolloid. Zeitsch.*, 1916, **18**, 11—16).—The author discusses certain apparently well-established cases of osmosis in which the solutions separated by the semi-permeable membrane are isosmotic, or in which the direction of the flow of water is from the more concentrated to the less concentrated solution (negative osmosis). It is supposed that these anomalous effects are due to electro-endosmose under the influence of local electric currents. Electro-endosmotic effects of this kind may occur when the membrane is permeable to the solvent as well as to electrolytes which may be present in solution, and also when the membrane is permeable to the solvent and to a particular ion. According to the explanation which is put forward, there is a close similarity in the relation between electro-endosmose and abnormal osmosis on the one hand, and between electrostenolysis and the Becquerel phenomenon on the other. In other words, the Becquerel phenomenon is attributable to electrostenolysis under the influence of local currents. H. M. D.

Diffusion of Iodine in Potassium Iodide Solutions. GRAHAM EDGAR and STERLING H. DIGGS (*J. Amer. Chem. Soc.*, 1916, **38**, 253—259).—The authors have determined the rate of diffusion of iodine into potassium iodide of various concentrations by the two-layer method. A layer of potassium iodide of concentration $0{\cdot}5N$, $0{\cdot}25N$, N, $2N$, $3N$, or $4{\cdot}5N$ was placed in a cylindrical vessel, and below it a layer of $N/20$-iodine in potassium iodide of the same concentration as the upper layer was introduced by means of a funnel. The amount of iodine which diffused into the upper layer was determined by titration with sodium thiosulphate. Viscosity measurements were made of solutions of iodine of the same concentrations and the fluidity calculated. It is shown that increase in the concentration of potassium iodide causes a marked increase in the rate of diffusion of the iodine; there is also an increase in the fluidity of the solutions. These results confirm the results of von Name (A., 1910, ii, 280; 1911, ii, 973) that the rate of reaction between iodine, in potassium iodide solution, and metals increases with increase in the concentration of the potassium iodide. Since these reactions depend on diffusion, it follows that von Name's results demand an increase in the rate of diffusion of iodine with increase in the concentration of potassium iodide. It is shown that the increased fluidity is insufficient to account for the increased rate of diffusion, and all other possible reasons would lead to a decreased rate of diffusion. J. F. S.

Non-ideal Solutions. The Activity of a Sparingly Soluble Component. E. K. STRACHAN (*J. Amer. Chem. Soc.*, 1916, **38**, 626—632).—A theoretical paper, in which the partial pressure of a sparingly soluble component (iodine) has been calculated from its partition-coefficient in pairs of binary mixtures, water and

carbon tetrachloride, carbon disulphide, and bromoform. The partial pressure of a sparingly soluble component of a truly non-ideal solution is expressed by the relationship

$$p=(N/N_s)p_0+C(N_s-N).N,$$

in which p is the partial pressure of the dissolved substance when its molecular fraction is N, p_0 is the vapour pressure of the pure solute, and N_s its molecular fraction in a saturated solution. C is a constant which is approximately inversely proportional to the square of the solubility of the dissolved substance. J. F. S.

A Theory of Multiple Ionisation. A Modification of the Electrolytic Dissociation Theory. FRANCIS FARHAM HEYROTH (*J. Amer. Chem. Soc.*, 1916, **38**, 57—65).—A theory of ionisation is proposed which brings into line a number of points which do not readily come under the Arrhenius dissociation theory. It is suggested that all electrolytes are amphoteric and ionise in two ways, the ratio between the two forms of ionisation, as expressed by their ionisation constants, varying from 1 : 1 to very nearly 1 : ∞, and depending on the nature of the solvent, the concentration of the solution, and the average structure of the molecules dissociating. Thus for nitric acid it is assumed that the dissociation occurs according to the equations $HNO_3 \rightleftarrows H^{\cdot}+NO_2{}'$ and $HNO_3 \rightleftarrows OH'+NO_2{}^{\cdot}$, the degree of dissociation being given by $\alpha+\beta=(i-1)/(n-1)$, in which α and β are the degrees of dissociation of the two schemes. On the basis of this theory the author explains the oxidising action of sulphuric and nitric acids. In the case of the solution of copper by hot concentrated sulphuric acid it is suggested that the two equilibria exist, $H_2SO_4 \rightleftarrows SO_4{}''+2H^{\cdot}$ and $H_2SO \rightleftarrows SO_2{}^{\cdot\cdot}+2OH'$, and that the $SO_2{}^{\cdot\cdot}$ is discharged on the copper, converting it into copper ions with the liberation of the gas. Explanations are also offered for the precipitation of silver and mercury oxides by sodium hydroxide, for the heat of neutralisation of weak acids and bases, and for the existence of acid chlorides, such as SO_2Cl_2. The bearing of the theory on the Ostwald dilution law is discussed. J. F. S.

Crystallographic Relations of Allied Substances Traced by Means of the Law of Valency-volumes. W. BARLOW (*Min. Mag.*, 1916, **17**, 314—323).—The equivalence-parameters of several pairs of sulphates (for example, $CuSO_4$ and $MgSO_4,H_2O$, $CaSO_4$ and $CaSO_4,2H_2O$, etc.) are compared. By suitably selecting the axes, it is found that two of the parameters are nearly equal for the two members of the pair, whilst the third parameter has the ratio of $W : W_2$, that is, the ratio between the sums of the valency-volumes of the two salts. From this it is concluded that there is a statification of the crystal-structure, the atomic arrangement in layers in one plane direction being the same for both salts of the pair. L. J. S.

Crystals as Molecular Compounds. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1915, **92**, 376—380).—When Bragg's structure for

the crystal of sodium chloride is examined, it is found that each sodium atom is symmetrically surrounded by six chlorine atoms and each chlorine atom by six sodium atoms. This accords with a co-ordination number of 6 for each of these kinds of atoms, the union being partly by principal and partly by subsidiary valences. This is in accordance with the structure of such salts as $[IAg_2]NO_3$, $[IAg_3](NO_3)_2$, $[PAg_6](NO_3)_3$, and $[AsAg_6](NO_3)_3$. In the case of symmetrical compounds, the difference between principal and subsidiary valences disappears. C. H. D.

The Crystallisation of Phenyl Ether. C. DAUZÈRE (*Compt. rend.*, 1916, **162**, 385—387).—The author has followed, by microscopic examination, the steady crystallisation of superfused phenyl ether at 20°, when a small fraction of the solid material is introduced into the liquid. The surface of the crystalline fragment introduced, which is generally very irregular, soon becomes regular by "cicatrisation" (compare Maurain, "Les états physiques de la matière," p. 92). This and the further growth of the crystal sets up two sorts of movements in the liquid. The first is a flow of the liquid towards the crystal which is manifest throughout the whole mass and produces eddies near the crystal. The second is of an undulating nature at the surfaces of contact between the liquid and the solid. It consists in a series of fine striata which pass continually along the growing faces, and are termed waves of crystallisation. These bring about the "cicatrisation" of the irregular crystals, and cause the formation of the faces and edges of the small crystals, the edges being the lines of stoppage of the undulatory movement, the stoppage being produced by an inverse undulation or by some other cause. W. G.

The Growth of Crystals. PAUL GAUBERT (*Compt. rend.*, 1916, **162**, 471—473. Compare *Bull. soc. franc. min.*, 1902, **25**, 258; 1904, **27**, 233).—A claim for priority over Dauzère (compare preceding abstract) for the discovery of the various movements of the liquid towards the crystal during crystallisation of a fused salt.
W. G.

The Mode of Flow in Crystalline Solids. G. TAMMANN (*Zeitsch. anorg. Chem.*, 1915, **92**, 37—46).—The view that the flow of crystalline solids is due to a partial melting is criticised. According to Poynting, the melting point of a solid is always lowered by pressure applied in such a way that the liquid formed is free to escape. This conclusion is due to a wrong application of thermodynamical reasoning to a case in which the cycle is not reversible. It is improbable that a characteristic property, such as the melting pressure, should vary with a chance condition such as the permeability of the wall of the containing vessel. The similar conclusion of Ostwald, derived from considerations of vapour pressure, is due to a misunderstanding of the space model containing the equilibrium curves.

Niggli (A., 1915, ii, 242) reached the same conclusion by con-

sidering the thermodynamical potential. This is also attributed to the application of a principle to a case in which it is invalid. The actual influence of compression or tension on crystals in equilibrium with their melt is so small as to be negligible, even when the stress applied approaches the elastic limit. This is confirmed by observation. C. H. D.

Colloidal Solid Solutions. D. McIntosh and R. Edson (*J. Amer. Chem. Soc.*, 1916, **38**, 613—615).—When a solution of a salt in water is plunged into a bath at a very low temperature the mass freezes as a whole and the frozen mass is homogeneous. Such solid masses the authors term colloidal solid solutions. The frozen material resembles ice, but is more opaque and not so hard; when examined microscopically it is seen to be homogeneous, and if the solid is allowed to melt undisturbed there is a clear solution formed. Hence in comparison with cryohydrate these solutions are reversible. On melting, these solutions have the exact temperature at which they would be in equilibrium with ice. These solutions conduct electricity, and the conductivity of 10%, 20%, and 30% solutions of potassium iodide has been determined at temperatures from $-80°$ to $-10°$. The conductivity shows a maximum rate of increase at $-21°$, that is, at the cryohydric temperature. Similarly, solutions of N, $N/2$-, and $N/4$-hydrochloric acid have been determined. The conductivity increases fairly regularly with increase of temperature. The conductivities of the acid solutions are much above those of salt solutions of the same concentration. J. F. S.

Effect of Freezing on Certain Inorganic Hydrogels. H. W. Foote and Blair Saxton (*J. Amer. Chem. Soc.*, 1916, **38**, 588—609).—A method is described by which the free, capillary, and combined water in gels may be determined, and consequently the composition of the hydrogel deduced. The method consists in cooling the hydrogel in a dilatometer filled with light petroleum to $-20°$ or $-30°$, and observing the motions of the thread. In carrying out a determination, the dilatometer readings at first show a regular decrease as the temperature falls, due to contraction of the bulb and its contents. At a temperature several degrees below zero sudden expansion occurs, due to freezing. The water freezing in this first expansion consists of free water and that part of the capillary water which has reached its freezing point. After the volume has become constant, a further lowering of temperature causes more capillary water to freeze, and the volume usually expands somewhat further, after which contraction sets in, and if the temperature is sufficiently lowered the contraction becomes very nearly a linear function of the temperature as it is before freezing occurs. The reverse of these changes occurs on warming. A number of preliminary determinations were carried out with sand and water, and lampblack and water for the purpose of testing the method and observing the difference between the behaviour of free and capillary water. Experiments were then carried out with the hydrogels of silica, alumina, and ferric oxide. In each case the

total water content was known, and from the expansion on freezing the free and capillary water could be calculated. Hence the water actually in combination in the hydrogel could be deduced. In the case of alumina, a sample with a total water content of 38·18% was shown to contain all its water in the combined condition. The effect of ageing and repeated freezing on the gel is investigated. In the case of silica two results are obtained which correspond with an amount of combined water agreeing with the formulæ $SiO_2,1{\cdot}31H_2O$ and $SiO_2,1{\cdot}35H_2O$. In the case of ferric oxide the amount of water remaining unfrozen corresponds with $Fe_2O_3,4{\cdot}25H_2O$. J. F. S.

Protective Colloids. Cetraria Islandica as Protective Colloid. I. Colloido-chemical Investigation of the Extract from Iceland Moss. A. GUTBIER, A. IRION and E. SAUER (*Kolloid. Zeitsch.*, 1916, **18**, 1—11).—The preparation of aqueous extracts containing colloidal substances from Iceland moss is described. These colloids, which are precipitated on the addition of alcohol to the aqueous extract, are characterised by great stability, and in the dry condition can be kept without change for an indefinite time. By means of viscosity measurements the authors have investigated the influence of high temperatures, hydrochloric acid, sodium hydroxide, and sodium chloride on the stability of the colloidal solutions, with the result that the solutions are found to exhibit only slight changes under the influence of these agents. The colloidal particles are negatively charged, and coagulation takes place at the anode. H. M. D.

Theoretical Study of Chemical Equilibrium. L. GAY (*J. Chim. phys.*, 1915, **13**, 402—413).—A discussion of the displacement of equilibrium resulting from the addition of one of the reacting substances to the system in equilibrium, by making use of the conception of the expansibility tension. H. M. D.

Non-, Uni- and Bi-variant Equilibria. VI. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1175—1190. Compare this vol., ii, 180).—A theoretical paper, in which the relation between the concentration– and pressure–temperature equilibrium diagrams is discussed. The two correspond in the sense that the one is a schematical representation of the other. H. M. D.

The Mechanism of Reactions in Aqua regia. E. BRINER (*Compt. rend.*, 1916, **162**, 387—389).—A study of the conditions governing the equilibrium of the reversible reaction:

$$HNO_3 + 3HCl \rightleftharpoons NOCl + Cl_2 + 2H_2O.$$

The equilibrium pressure at 0° is 2·84 atmos. and at 20·5—21° it is 5·1 atmos. Within the limits studied, the system is univariant, having three phases and two independent components. One liquid phase consists of nitrosyl chloride and chlorine in equilibrium with the aqueous phase, which contains, in addition to the original acids,

some chlorine and nitrosyl chloride. The gaseous phase contains all the constituents of the system. If the acids used are too dilute the phase consisting of the liquefied gases does not exist, and the equilibrium pressures diminish as the dilution increases. If the two concentrated acids are mixed in a Dewar vessel there is first a rapid rise of several degrees in the temperature, which then descends steadily and remains constant at about 2° below the original temperature of the acids. The preliminary rise in temperature is due to the action of the hydrogen chloride on the water of solution of the nitric acid. Taking into account the heats of solution, the heat of the reaction, using 37% hydrochloric acid and 70% nitric acid, is -20 Cal., and if the dilution of the acids is double the value, is -27 Cal. W. G.

The Law of Mass Action as a Special Case of a General Reaction Law. H. J. PRINS (*Chem. Weekblad.*, 1916, **13**, 344—350).—A theoretical paper, dealing with the phases of chemical reaction and the conditions governing it. A. J. W.

Partition Coefficients of Hydrogen Peroxide between Water and Certain Organic Solvents. JAMES H. WALTON and HAROLD A. LEWIS (*J. Amer. Chem. Soc.*, 1916, **38**, 633—638).—The partition-coefficient of hydrogen peroxide between water and each of the following liquids has been determined at 25°: ethyl acetate, *iso*butyl alcohol, amyl alcohol, acetophenone, ethyl ether, and aniline. It is shown that those organic solvents which will dissolve water will also dissolve hydrogen peroxide. Hydrogen peroxide does not undergo association in any of the above-named solvents. The values obtained by the authors in ethyl ether solution do not agree with those of Osipov and Popov. Hydrogen peroxide is soluble in phenol and in quinoline. The solution in quinoline is not one of simple peroxide molecules, but probably consists of a compound of the solvent and hydrogen peroxide in equilibrium with hydrogen peroxide. Quinoline is an unusually good solvent for hydrogen peroxide. At 0° for certain concentrations of hydrogen peroxide the ratio, H_2O_2 in water/H_2O_2 in quinoline, may be as low as 0·276. J. F. S.

Distribution of Caffeine Sodium Salicylate. RAPHAEL ED. LIESEGANG (*Kolloid. Zeitsch.*, 1915, **16**, 13—16).—It has been found that the gelatinous residue, which is obtained by evaporation of a few drops of a solution of caffeine sodium salicylate on a glass plate, shows a well developed banded structure. If a concentrated solution of the double salt is heated on a water-bath, a similar distribution in layers of different refractive index is observed. The phenomenon, which appears to be dependent on the existence of a temperature gradient in the solution, has also been observed with solutions of gelatin and in lesser degree with solutions of sodium chloride, magnesium chloride, and sodium silicate. H. M. D.

Dynamics of Scission of Carbon Dioxide from Organic Compounds. EMIL BAUR and R. ORTHNER (*Zeitsch. physikal. Chem.*, 1916, **91**, 75—102).—The authors have studied the action of heat

on substances which evolve carbon dioxide, with the object of ascertaining whether these reactions are in accord with the law of mass action and are reversible. The three cases studied were: (i) the decomposition of basic ferric oxalate into ferrous oxalate and carbon dioxide, (ii) salicylic acid into phenol and carbon dioxide, and (iii) sodium salicylate into sodium phenoxide and carbon dioxide. It is shown in the case of basic ferric oxalate that an equilibrium is set up at temperatures between 160° and 200°; the equilibrium pressure was measured, and the mass action constant deduced. In the case of salicylic acid the mass-action constant was found to be $2{\cdot}7 \times 10^{-4}$ at 203°; the dissociation pressure of sodium salicylate at 220° and 230° was found to be 143 mm. and 183·5 mm. respectively. In no case could the equilibrium value be obtained from the other side, even when carbon dioxide, at pressures considerably above the dissociation pressure, was employed. The three cases investigated therefore represent reactions which proceed to an equilibrium that can only be obtained from one side, that is, they are reversible reactions since they follow the law of mass action, but the equilibrium can only be approached from one side. J. F. S.

Effect of Dissolved Substances on the Velocity of Crystallisation of Water. JAMES H. WALTON and ALBERT BRANN (*J. Amer. Chem. Soc.*, 1916, **38**, 317—330. Compare A., 1915, ii, 15). —In a previous communication the linear velocity of crystallisation of water supercooled to $-9°$ was measured. Using the same method, the effect of dissolved substances on the velocity of crystallisation of water supercooled to $-9{\cdot}1°$ has been determined for forty-five substances, which include organic substances such as sucrose, carbamide, dextrose, mannose, glycerol, ethyl alcohol, lævulose, antipyrine and raffinose, and a number of the commoner inorganic acids, salts, and bases. The dissolved substances all retard the velocity of crystallisation. Solutions of equimolecular concentration show different retarding effects. The retardation is not, therefore, a colligative property. For substances with more than eight atoms in the molecule there is a rough relation between the number of atoms in the molecule and the inhibition of the velocity of crystallisation; the greater the number of atoms the slower the rate. For compounds with less than eight atoms the power of retardation seems to be a specific property. That these effects cannot be explained by Marc's adsorption theory of the inhibition is evidenced by the fact that the sugars which are not greatly adsorbed are very active in retarding the rate of crystallisation. Certain inorganic salts also show no relation between the extent to which they are adsorbed and their retardation of the formation of ice crystals. Substances in the colloidal state, such as gelatin, ferric hydroxide, and certain dyes, retard the velocity of crystallisation. The stability of the supercooled solutions toward spontaneous crystallisation varies with the dissolved substance. Solutions of *N*/10-hydrochloric acid are exceptionally stable. Dilute solutions of certain dyes are also unusually stable. Solutions of brucine sulphate with a con-

centration less than 0·00125 gram.-mol. per litre do not affect the velocity of crystallisation. These solutions, however, are much more stable toward spontaneous crystallisation than pure water at the same temperature. J. F. S.

Velocity of Vaporisation of Liquids. M. Le Blanc and G. Wuppermann (*Zeitsch. physikal. Chem.*, 1915, **91**, 143—154).—The experiments of Winkelmann (*Ann. Phys. Chem.*, 1884, [ii], **22**, 1) on the connexion between velocity of vaporisation and velocity of diffusion have been repeated both in glass and in metal tubes. It is shown that the increase in the diffusion-coefficient with increasing diffusion height in the case of vapours is due to the decreasing temperature lowering at the surface of the evaporating liquid. When this temperature lowering is avoided it is shown that for water, ethyl alcohol, benzene, chlorobenzene, and propyl acetate the quantity evaporated per unit of time, other conditions being constant, is inversely proportional to the length of the diffusion height and that the coefficient of diffusion remains constant. The velocity of vaporisation is therefore, at the temperatures investigated (42—67°), conditioned by the velocity of diffusion.
J. F. S.

The Velocity of Hydration of the Anhydrides of some Fatty Acids. II. P. E. Verkade (*Rec. trav. chim.*, 1916, **35**, 299—308. Compare Böeseken and Verkade, A., 1914, ii, 256).—The velocities of hydration of two mixed acid anhydrides have been measured at 25° by the conductivity method, and the unimolecular velocity-coefficients have been calculated. The values obtained for 0·4343k at 25° were for acetic propionic anhydride 0·0524, and for *n*-butyric *iso*propylacetic anhydride 0·0155. The influence of ionisation has been eliminated by dividing these hydration-coefficients by the mean of the ionisation-coefficients of the corresponding acids. The results obtained bear out the previous deductions (*loc. cit.*).
W. G.

Action of Salts with Water of Hydration and without Water of Hydration on the Velocity of Saponification of Esters. J. E. L. Holmes and Harry C. Jones (*J. Amer. Chem. Soc.*, 1916, **38**, 105—121).—Jones and Guy (*Ann. Physik*, 1914, [iv], **43**, 555) have shown that combined water is more transparent to light than water in the free condition. The present paper deals with experiments which show that combined water is more active in effecting saponification than free water. The rate of saponification of methyl acetate and methyl formate has been carried out in water solution and in solutions of potassium chloride, potassium nitrate, calcium chloride, magnesium chloride, strontium chloride, lithium chloride, sodium chloride, calcium nitrate, sodium nitrate, sodium bromide, potassium bromide, barium chloride, magnesium nitrate, potassium iodide, sodium iodide, lithium sulphate, and lithium nitrate at temperatures of 15°, 25°, and 35°. The solutions of the salts were N, $N/2$, and $N/4$. The plan of work adopted was to investigate the difference in the velocity with which free water

and combined water effect the saponification under the following conditions: (i) Time and concentration constant with varying temperature. (ii) Concentration and temperature constant with varying time, and (iii) time and temperature constant with varying concentration. The amount of saponification was determined by titrating measured quantities of the solution by means of a solution of ammonia, using corallin as indicator. The salts, magnesium chloride, calcium chloride, strontium chloride, barium chloride, magnesium nitrate, calcium nitrate, and strontium nitrate produce the largest increase in the velocity of saponification, and these salts are all hydrated. Then come the non-hydrated salts sodium chloride, sodium nitrate, potassium chloride, and potassium bromide. Along with these, however, the hydrated salts sodium bromide, calcium bromide, lithium chloride, lithium bromide, lithium nitrate, and magnesium bromide also appear. The salts lithium sulphate, sodium iodide, strontium bromide, lithium bromide, and potassium iodide give smaller velocities than pure water. On dilution, the effect with salts having water of crystallisation decreases more rapidly than with salts which have no water of crystallisation, which shows that the saponification cannot be due to the hydrolysis of the salts alone. The large effect with salts with water of crystallisation is probably due, in part, to their being hydrated, combined water being more highly ionised than free water. The amount of saponification seems to be due to the combined effect of both cation and anion. There is a definite dilution for each salt at which the maximum saponification occurs. Hydrated salts show a large temperature-coefficient, notwithstanding the decomposition of hydrates with rise of temperature, probably due in part to hydrolysis.

J. F. S.

The Velocity of Saponification of Fats and Oils by Potassium Hydroxide in Different Solvents. ERNEST ANDERSON and H. L. BROWN (*J. Physical Chem.*, 1916, **20**, 195—213).—The scope of the work was the determination of the order of the reaction, the relative velocity of saponification of different oils and fats, the influence of the solvent and of temperature. The different solvents used were methyl, ethyl, and amyl alcohols, and the oils included cotton-seed, castor, olive, and croton, with butter fat. Check experiments were made with methyl acetate, which is known to be hydrolysed according to a bimolecular law. In every case the saponification of the glyceride was found to be a bimolecular reaction, and all the fats and oils studied were saponified at approximately the same rate, although this appeared to increase slightly with the molecular weight of the fatty acid. The following constants were obtained by saponifying 5 c.c. of the glyceride in 200 c.c. 0·2*N*-amyl alcoholic potash:

Oil.	Cotton-seed.	Croton.	Olive.	Castor.
Mol. wt.	274	279	291	293
Vel. const.	0·001550	0·001578	0·001605	0·001692

The velocity constant in amyl alcohol ($D^{15\cdot5}$ 0·8140) is twice as great as in ethyl alcohol ($D^{15\cdot5}$ 0·8171) and about ten times as great

in this as in methyl alcohol ($D^{15\cdot5}$ 0·8100). An increase in water content of the alcohol causes an increase in the velocity constant when methyl alcohol is the solvent. In ethyl alcohol the temperature-coefficient of the reaction velocity between 15° and 25° is 2·36 for castor oil. The velocity is increased by increasing the concentration of the alcohol, but the increase is not the same in alcohols of different strengths. The effect of increasing the concentration of the oil differs in different solvents, and in amyl alcohol actually decreases the reaction velocity. E. H. R.

Influence of Neutral Substances on the Rate of Change in Jellies. RAPHAEL ED. LIESEGANG (*Kolloid Zeitsch.*, 1916, **18**, 16—18).—Experiments are described which show that the rate of interaction of two substances, one of which is present in a gelatin jelly and the other in a superimposed aqueous solution, is not in general affected by the presence of neutral substances in the aqueous solution. In other words, the osmotic pressure of the aqueous solution is not a determining factor in reactions which take place under the special conditions referred to. A study of the progress of such diffusion reactions has shown that the initial stages are characterised by a relatively high velocity for which no explanation has as yet been found. H. M. D.

Catalysis. I. NILRATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1084—1096).—Experiments have been made with supersaturated solutions of various substances in order to ascertain whether crystallisation is induced by the addition of isomorphous substances. No change was observed in supersaturated calcium chloride solutions on the addition of calcium fluoride or strontium chloride ($SrCl_2,6H_2O$). Copper sulphate solutions were unaffected by the addition of the crystalline sulphates of magnesium, manganese, iron, cobalt, zinc, and cadmium. Cobalt sulphate and magnesium sulphate solutions containing up to 50% of salt in excess of that corresponding with the saturated solutions were also unaffected by the addition of crystals of the above isomorphous salts. Sodium selenate crystals produced no effect on supersaturated sodium sulphate solutions, and the same result was obtained on the addition of sodium nitrate to supersaturated solutions of silver nitrate. The supersaturation of benzoic acid solutions was unaffected by the addition of crystals of salicylic acid, and, conversely, benzoic acid crystals were without influence on supersaturated solutions of salicylic acid.

The results obtained are not in harmony with the frequently expressed opinion that induced crystallisation affords a means of identifying isomorphous substances. H. M. D.

Catalysis. II. NILRATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1097—1133).—The influence of light on the velocity of a number of reactions has been examined by making parallel observations in the dark and in diffused light or sunlight. The reactions examined include the action of bromine on aqueous

solutions of various organic acids and their salts, of bromine on ethyl and methyl alcohols, of sodium persulphate on aqueous solutions of bromides, of iodine on aqueous solutions of nitrites, hydrazine hydrochloride, hydroxylamine hydrochloride, hypophosphorous acid and its salts and acetone. Other reactions include the reduction of mercuric chloride and auric chloride by organic acids and their salts, and the reduction of potassium permanganate by various organic acids. In all cases, the reaction velocity was found to be greater under the influence of light.

The reaction between iodine and oxalates, $I_2 + M_2C_2O_4 = 2MI + 2CO_2$, where M represents ammonium or potassium, would seem to afford a possible basis for actinometric measurements. The rate of the reaction is not influenced to an appreciable extent by either oxygen or carbon dioxide. H. M. D.

Catalytic Oxidation of Hypophosphite Solutions by Palladium. A. Sieverts and E. Peters (*Zeitsch. physikal. Chem.*, 1916, **91**, 199—231).—The conditions under which various forms of palladium effect the catalytic oxidation of hypophosphite solutions, as well as the kinetics of the process, have been investigated at various temperatures. The progress of the oxidation was followed both by titration of the solutions with iodine and by measurement of the volume of hydrogen liberated. It is shown that aqueous solutions of sodium hypophosphite under the influence of palladium evolve hydrogen according to the equation:

$$NaH_2PO_2 + H_2O = NaH_2PO_3 + H_2.$$

A further oxidation to phosphate also takes place according to the equation: $NaH_2PO_3 + H_2O = NaH_2PO_4 + H_2$. The velocity of the second reaction is small, and it can generally be neglected in measurements of the velocity of the first reaction, which is high, particularly if an excess of hypophosphite is present. All kinds of palladium are not active in this reaction; palladium-black is active, irrespective of its method of formation. Ignited palladium sponge is slightly active, but wire and foil are inactive, even though they are charged with hydrogen. If the metal is superficially oxidised it is reduced by the hypophosphite and at once becomes active. The commencement of the catalysis is not dependent on the hydrogen content of the palladium. Palladium, which has been electrolytically deposited on platinum or copper gauze, slowly loses its activity in a solution of hypophosphite. The experiments on the velocity of the oxidation were all carried out with palladium-black. The initial velocity of the reaction is given by the equation $-dc/dt = k'c^{0\cdot18}$, in which c is the concentration and k' is a constant. In one and the same experiment the velocity is disturbed because the catalyst loses some of its activity. The acid phosphite formed in the reaction has no marked influence on the velocity. The temperature-coefficient between 15° and 32° is that of a chemical reaction. The rate of stirring of the reaction mixture has little influence on the velocity. The quantity of hypophosphite oxidised in a given time is proportional to the weight

of the catalyst present. The addition of hydrochloric acid, sulphuric acid, or sodium hydroxide retards the reaction, whilst the addition of sodium hydrogen carbonate either slightly accelerates the reaction or has no influence. The activity of colloidal palladium is very much greater than that of palladium-black, but the reaction in both cases proceeds according to the same laws. The expression giving the time-velocity equation is deduced from the assumption that the velocity of reaction is proportional to the quantity of hypophosphite adsorbed by the palladium, and that the adsorption takes place with a velocity which is very large when compared with the velocity of the chemical reaction. J. F. S.

Kinetics of the Catalytic Oxidation of Phenylthiocarbamide by Charcoal. H. FREUNDLICH and ALF. BJERCKE (*Zeitsch. physikal. Chem.*, 1916, **91**, 1—45).—The oxidation of phenylthiocarbamide in solution by blood charcoal has been studied at 0°, 25°, and 35°, both with regard to the nature of the oxidation products and the kinetics of the process. The conclusions reached have been considered in connexion with enzyme reactions. The kinetics of the oxidation of oxalic acid by blood charcoal have also been experimentally studied. It is shown that the decomposition of phenylthiocarbamide by charcoal consists in an oxidation whereby sulphur is liberated and a basic organic substance formed. This basic substance, whilst not definitely characterised, is shown to be probably the so-called Hector base, the process being regarded as following the equation:

$$2NH_2\cdot CS\cdot NHPh + O_2 = NH\begin{cases} C(NPh)\cdot S \\ C(NH)\text{—}NPh \end{cases} + 2H_2O + S.$$

The velocity of the reaction is given by the equation:

$$dx/dt = k\,.\,m_0/v_0[\sqrt{(O_2)_L}/(x+\xi)],$$

which on integration gives $k = v_0/2m_0t[(x+\xi)^2/\sqrt{(O_2)_L}]$. In these equations x is the decrease in the concentration of phenylthiocarbamide in the time t, m_0 the original quantity of charcoal, v_0 the original volume, $(O_2)_L$ the constant oxygen pressure during the experiment, ξ is the decrease in concentration of the phenylthiocarbamide from the beginning of the experiment to the time when the first quantity is removed for analysis—that is, it is the quantity of phenylthiocarbamide removed in the time required for the adsorption to complete itself; k is a constant. Consequently, the velocity of the reaction is proportional to the square root of the oxygen concentration, to the relationship m_0/v_0, and inversely proportional to the quantity of phenylthiocarbamide changed per unit weight of charcoal. The temperature-coefficient of the reaction is fairly large, $k_{35°}/k_{25°} = 2\cdot3$, and is in keeping with the Arrhenius formula. The singular kinetic progress of the reaction can be readily explained by the assumption that the reaction depends on diffusion phenomena, the phenylthiocarbamide being strongly adsorbed by the charcoal whilst the oxygen diffuses into it through a layer of the decomposition products which surround the charcoal

particles. This assumption is not at variance with the high temperature-coefficient, because the equilibrium constant not only represents the diffusion constant, but also other quantities which are influenced by temperature, for example, the solubility of oxygen in the diffusion layer. The adsorption of phenylthiocarbamide is in accordance with the adsorption isothermals, and decreases with increase of temperature. The oxidation of oxalic acid by blood charcoal can also be regarded as a diffusion process, and here again it is the oxygen which diffuses into the charcoal. In this case the products of the reaction, water and carbon dioxide, are without influence, the diffusion layer in this case consisting of adsorbed oxalic acid, which retards the reaction according to the equation $-dc/dt=k'.1/c^{1/n}$, which on integration yields $(1+1/n)k'=k=1/t(c_0^{1+1/n}-c^{1+1/n})$. In this equation c_0 is the initial concentration of the oxalic acid, c the concentration at time t, and $1/n$ the index of the adsorption isothermal of oxalic acid. The equation representing the velocity of the oxidation of phenylthiocarbamide agrees with the Schütz rule for enzyme reactions. When it is considered that the oxygen remains constant during the operation, and that in enzyme reactions v_0 is constant, it follows that these quantities can be taken into the constant, and the equations then become: $(x+\xi)^2=x.m_0t$ or $x+\xi=x'\sqrt{m_0t}$. To bring the present case into line with the Schütz rule it is therefore only necessary to substitute enzyme concentration by charcoal concentration.

J. F. S.

Catalytic Reduction in the Presence of Platinum and Palladium. J. Böeseken [with (Mlle.) O. B. van der Weide and C. P. Mom] (*Rec. trav. chim.*, 1916, **35**, 260—287).—A quantitative study of the reduction of a number of unsaturated acids, using as catalysts palladium and platinum prepared in different ways, and used in varying amounts. Working with a very stable form of palladium, prepared according to the method of Paal (compare A., 1905, ii, 397), and studying the reduction of crotonic acid, it was found that there was a certain relationship between the velocity of absorption of the hydrogen and the number of shakes per minute until the latter reached 160, when the absorption became independent of the shaking. Similar results were obtained with *iso*crotonic and tetrolic acids. In the case of substances containing more than one double bond, no break was found in the absorption curves when the first molecule of hydrogen had been absorbed. In the case of trichloroacrylic acid after the fixation of 1 molecule of hydrogen, the absorption still continued regularly, the chlorine atoms thus being removed with almost the same velocity as that with which the molecule of hydrogen was fixed by the unsaturated linking. In the case of oleic acid, the absorption of hydrogen is not complete, probably owing to the formation of a soap which checks the action of the catalyst.

Working with a less active and less stable form of catalyst, a comparison was made of the reduction of muconic, aconitic, itaconic, citraconic, mesaconic, *cyclo*propane-1 : 1-dicarboxylic,

ethylenetricarboxylic, and vinylglycollic acids. Of these, all but the first- and last-named gave negative results. These acids were, however, very slowly hydrogenated, using a palladium catalyst prepared by Skita's method (compare A., 1913, i, 53). The results obtained indicate that an accumulation of carboxyl groups around the double linking prevents the reduction, or if it takes place, the velocity is dependent more on the physical state of the catalyst and the solution than on the free energy of the reaction.

The velocity of reduction of cinnamic acid in the presence of finely divided platinum shows a sudden diminution after the side-chain is saturated, the benzene ring being apparently hydrogenated more slowly. The reduction then proceeds regularly until three more molcules of hydrogen have been added, when there is a further diminution in the velocity of the action. This is a physical effect, since an increase in the amount of catalyst used lessens the difference between the velocities of hydrogenation of the side-chain and the nucleus.

The state of the surface of the catalyst principally controls the reduction, since a preliminary boiling of the catalyst with acetic acid considerably reduces the action, whilst exposure to a mercury lamp for twenty minutes considerably increases the velocity of absorption of the hydrogen. W. G.

Baly's Theory of Chemical Reaction and Reactivity. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1916, **38**, 1—15).—Polemical. A criticism of Baly's theory of chemical reaction and reactivity (T., 1904, **85**, 1029; A., 1915, ii, 440). J. F. S.

[Baly's Theory of Chemical Reaction and Reactivity.] A Reply to Dr. Dehn. E. C. C. BALY (*J. Amer. Chem. Soc.*, 1916, **38**, 15—20, 227—228).—Polemical. A reply to Dehn's criticism (see preceding abstract). J. F. S.

Conception of Element and Atom in Chemistry and Radiology. FRITZ PANETH (*Zeitsch. physikal. Chem.*, 1916, **91**, 171—198).—A theoretical paper, in which the conception of the terms atom and element is discussed. It is shown that the discovery of radioactive disintegration, isotopy, and the linear system of the elements of Moseley make it imperative that the definitions of atom and element should be revised. In the literature of radioactivity, isotopes are regarded as different elements; this practice makes the conception of an element in chemistry quite meaningless, because the law of the immutability of the elements must be given up and the number of the chemical elements will become exceedingly large. It appears, therefore, more practical to regard isotopes, not as different elements, but as varieties of one and the same element. This will be in accord with the Boyle definition of an element, which will then only need extending by the phrase: "That two substances which are non-separable are to be regarded as the same element." The definition, therefore, proposed for an element is

as follows: "An element is a substance which cannot be simplified by any chemical process." Substances which fulfil this condition must therefore be regarded as one and the same element if after being mixed they cannot be again separated. Atoms are those ultimate particles of matter which represent the limit of chemical division, and are themselves unchanged by chemical processes. In connexion with these definitions the following properties and facts are fundamental: (1) The number of chemical elements is 92, and of these 5 have not yet been discovered. (2) Every element is characterised by its chemical and electrochemical properties, by its spectrum and *X*-ray spectrum, and by its nuclear charge. (3) Atomic weight and radioactive properties are not constants of the elements. (4) There are more varieties of atoms than of elements. At the moment, 120 varieties have been identified; the number of varieties not yet discovered is unknown. An element can consist of similar atoms (pure elements) or of atoms differing in weight or radioactivity or both (mixed elements). Isotopic elements can completely represent one another in mass actions, so that in calculations in chemical and electrochemical experiments the concentration of a mixed element is to be regarded as the sum of the concentrations of the different varieties of atoms. The radioactive disintegration of an atom always leads to the production of an atom of a different element, but further disintegration can lead to an atom of the original element. J. F. S.

Atomic Structure. V. Periodic System and the Properties of the Elements. WILLIAM D. HARKINS and R. E. HALL (*J. Amer. Chem. Soc.*, 1916, **38**, 169—221).—A method of representing the periodic system graphically is described in the paper, in which the relationships between the elements of the main and sub-groups are clearly shown. The elements are arranged in the table in the exact order of their atomic numbers, and there are no blank spaces for unknown elements which do not correspond with atomic numbers as found by Moseley's work on the *X*-ray spectra of the elements. The elements are also plotted according to their atomic weights, so that the isotopic forms of an element may be shown graphically on the table, and the group changes occasioned by α- and β-ray decompositions of the radio-elements clearly depicted. Both the zero and eighth groups fit naturally into the system, the latter appearing as the sub-group of the former. The table is best represented as a helix in space, but may be shown as a spiral on a plane. The space form is represented by its vertical projection on a plane, but drawn with line perspective so that it may be easily visualised. Beginning at the zero group, the maximum positive valency of a group is found by counting toward the front and toward the right, Li=1, Be=2, etc., and the negative valency by counting toward the back, F=−1, O=−2, N=−3, etc. The elements in the table divide themselves into cycles: cycle 0; cycle 1, He–Cl, 16 elements = 4^2; cycle 2, 36 elements = 6^2, A–I; cycle 3, 64 elements = 8^2, Xe–U. The latter part of the third cycle is missing. Each cycle is divided into two periods; cycle 1 into first short period, $2 \times 2^2 = 8$ elements,

He–F, and second short period, Ne–Cl, $2 \times 2^2 = 8$ elements; cycle 2 into first long period $2 \times 3^2 = 18$ elements, A–Br, and second long period $2 \times 3^2 = 18$ elements, Kr–I; cycle 3 into first very long period $2 \times 4^2 = 32$ elements, Xe–EkaI, and second very long period, Nt–U. These relations are undoubtedly a numerical expression of a function connected in some way with the system according to which the nuclei of the elements have been built up. Whenever the valency drops in passing along the continuous line connecting the elements in order of their atomic numbers, it always drops by seven, either from seven to zero, I $\longrightarrow$ Xe, or from eight to one, Pt $\longrightarrow$ Au. In the latter case a certain sluggishness is evidenced in the drop, so that it is not entirely complete, and copper, silver, and gold, the members which should have a maximum valency of one, often exhibit a higher valency, such as two for copper and three for gold. The groups are arranged in the table in five divisions: 0 comprising groups 0 and 8; 1 comprising 1 and 7; 2 comprising 2 and 6; 3 comprising 3 and 5; and 4 comprising 4 and 4. The two groups of one division are said to be complementary. The sum of the group numbers of two complementary groups is always 8, as is also the sum of the maximum valencies. The algebraic sum of their characteristic valencies, on the other hand, is always zero. Thus the characteristic valency of group 1 is $+1$, that for group 7 is -1. The characteristic valency of the eighth group needs to be defined in this sense, and must be taken as -0, which accords with Abegg's valency system. Another very important relationship given graphically in this table and not elsewhere is that between the main and sub-groups in any one division. Whenever the groups in any one division differ considerably, as is the case in divisions 0 and 1, then the elements in the sub-groups are quite different chemically from those in the main groups, although in general they are alike in valency. As the group numbers approach each other in magnitude, the elements of the sub-group become chemically much more like those of the main group. This is true of groups 4*A* and 4*B*, where the group numbers are the same, and the two groups are practically indistinguishable in their general chemical nature. On the outer cylinder of the helix the main groups, 1, 2, 3, become less positive as the group number increases, whilst the corresponding sub-groups become more positive. Whenever the atomic volume of a main-group element is large, that of the corresponding sub-group element is small, and as the atomic volume of the main-group element decreases, that of the sub-group increases, until the values become about the same in groups 4*A* and 4*B*. The metals of the rare earths are put in the third group, since their valency is 3, and since if they are distributed around the table there are not enough known and undiscovered elements together to go round. Cerium may be classified either with the third or fourth group. A discussion on this point is given in the paper. The elements of the rare earths, exclusive of cerium and yttrium, decrease in their basic properties as the atomic weight increases, which is exactly the opposite of the general rule. In this case the atomic number increases, whilst the valency remains constant. On the other hand,

it seems probable that the atomic volume tends to change normally, but this tendency is masked by another tendency, which tends to keep the atomic volume constant. The metals of the rare earths lie on the front of the table, where the elements in general become less basic as the atomic weight increases, so they, in this respect, as probably they do with the atomic volumes, effect a compromise between this tendency and that which seeks to cause the elements in a single group to become more basic with increase in atomic weight. The resultant effect is that they become less basic as the atomic number increases, but not with anything like the rapidity which would be shown if they were to go round the table in the usual manner. In this sense the rare-earths group constitutes a group of its own, but a loop of practically constant valency. The table shows the relation between the properties of the elements and the nuclear charge, and this presumably is equal to the number of external electrons. It is probably the spacing and arrangement of these electrons which determine the chemical and most of the physical properties of the elements. The graphic representation of the table shows that the spiral forms a series of lines which in any part are very nearly parallel. This is a representation of the fact that the atomic weights increase in a very regular way in any one group and at about the same rate in all the groups. This regularity may be explained on the basis of the theory of Harkins and Wilson, that the nuclei of the elements are built up from the helium and hydrogen nuclei in a regular way, according to which the differences in mass in any one group are generally due wholly to differences in the number of helium nuclei present, at least in the case of the lighter elements. The radioactive elements fit into the system quite well. A discussion on the nature of isotopes is entered into. A number of tables and diagrams are included, which illustrate the connexion between the cohesional properties of the elements and the system. Curves are given of melting points, with lines of maxima and primary and secondary minima, atomic volumes, density, cubical-coefficients of expansion, compressibility, susceptibility, atomic frequency, elasticity, cohesion, and hardness. The causes of variations of cohesion are discussed. J. F. S.

The Formation of Molecules in its Dependence on Atomic Structure. W. Kossel (*Ann. Physik*, 1916, [iv], **49**, 229—362).—A theoretical paper in which the author develops the view that the properties of the atoms, and in particular the valency, are functionally related to the atomic numbers, and that the combination of atoms to form molecules is consequently determined by the structure of the atoms in accordance with the atomic number hypothesis. The application of the idea is considered in detail by reference to elements and groups of varying valency and widely different electrochemical character. H. M. D.

Large Fat Extractor. Carl L. A. Schmidt (*J. Ind. Eng. Chem.*, 1916, **8**, 165).—An apparatus suitable for extracting the fat from several pounds of material consists of a large distillation flask and

the extractor proper; the latter is a cylindrical vessel having a dome-shaped cover, which carries a reflux apparatus. A tubulure at the upper part of the side of the cylinder is connected by a glass tube with the flask, this tube allowing the vapour of the solvent to pass from the flask to the condenser, and the solvent collecting in the cylinder returns to the flask through a siphon tube extending from a tubulure at the bottom of the cylinder to the bottom of the flask. W. P. S.

Inorganic Chemistry.

The Solubility of Hydrogen in the Solid Alloys of Palladium with Gold, Silver, and Platinum. A. SIEVERTS, E. JURISCH, and A. METZ (*Zeitsch. anorg. Chem.*, 1915, **92**, 329—362).—Except for a few isolated measurements by Graham, the only determinations of the solubility of gases in solid alloys are those by Berry (T., 1911, **99**, 463), according to which the solubility of hydrogen in alloys of palladium and gold decreases regularly with increasing gold, becoming zero at 80% Au. In the present experiments the alloys are warmed to a constant temperature in an atmosphere of hydrogen at a given pressure. The measurements are made in the same way as with pure palladium (A., 1914, ii, 626). The range employed is from 138° to 820°, and from 1 atmosphere pressure downwards.

In all cases the solubility is proportional to the square root of the pressure, and, except in the platinum series, diminishes with increasing temperature. The addition of gold to silver first increases and then diminishes the solubility of hydrogen, the maximum occurring at lower concentrations of gold, the higher the temperature, until at 827° any addition of gold lowers the solubility. The isotherms of relative solubility also pass through a maximum at temperatures below 600°.

Although hydrogen is insoluble in pure silver, the addition of silver to palladium greatly increases the solubility, until a maximum is reached at all temperatures at 40% Ag, beyond which it again falls rapidly. At 138° an alloy containing 40% Ag dissolves more than four times as much hydrogen as pure palladium, the solubility becoming zero at 70% Ag. The relative increase of solubility in the case of an alloy containing 40% Ag increases with falling temperature until 270°, but diminishes as the temperature falls further.

Platinum in all proportions diminishes the solubility. The higher the temperature the less is the lowering of solubility produced by a given addition of platinum. At constant temperature the depression diminishes more slowly than the platinum content.

C. H. D.

Physical Constants of Chlorine. MAURICE PELLATON (*J. Chim. phys.*, 1915, **13**, 426—464).—Measurements have been made of the vapour pressure of liquid chlorine, of the orthobaric densities of liquid and saturated vapour, and of the critical constants. The chlorine used in the investigation was obtained by heating auric chloride.

The vapour-pressure measurements extending from $-78\cdot9^{\circ}$ up to the critical temperature can be represented by the formula $\log p = A - B/T - C \log T$, in which, when p is expressed in atmospheres, $A = 4\cdot922232$, $\log B = 2\cdot9676491$, and $\log C = -1\cdot8967405$. The critical temperature is $144\cdot0^{\circ}$, the critical pressure $76\cdot1$ atm., and the critical density $0\cdot573$. The ordinary b. p. is $-34\cdot5^{\circ}$.

The orthobaric densities are in satisfactory agreement with the law of the rectilinear diameter, and the density of liquid chlorine may be represented by the empirical formula:

$$d_l = a + b(144 - t) + c\sqrt{144 - t},$$

in which $a = 0\cdot687014$, $b = 0\cdot0002379$, and $c = 0\cdot0622109$. The same type of formula also represents the density of the saturated vapour, the values of the constants being $a = 0\cdot48219$, $b = 0\cdot002451$, and $c = 0\cdot068526$.

The heats of vaporisation of liquid chlorine at various temperatures have been calculated from the vapour pressure data. The ratio of the critical density to that calculated from the simple gas laws is $3\cdot635$, and the value of Trouton's constant is $20\cdot67$. These and other results indicate that chlorine behaves as a normal substance.

Measurements are also recorded of the dissociation pressure of auric chloride at temperatures between 140° and 260°. The pressure increases from $4\cdot5$ mm. at 140° to 931 mm. at 260°, and the variation with temperature can be expressed by the formula $\log p = A - B/T - C \log T$, in which $A = 51\cdot6852$, $\log B = 3\cdot841148$, and $\log C = 1\cdot117057$. H. M. D.

Oxidation of Hydrazine. VII. The Rôle of Nitrous Acid in the Formation of Azoimide. A. W. BROWNE and O. R. OVERMAN (*J. Amer. Chem. Soc.*, 1916, **38**, 285—302, and *Zeitsch. anorg. Chem.*, 1916, **94**, 217—239. Compare A., 1905, ii, 449; 1909, ii, 233, 658; 1911, ii, 1084, 1085).—A number of experiments on the oxidation of hydrazine and ammonia by various oxidising agents have been carried out. It is shown that no indication of the formation of appreciable quantities of nitrous acid or nitric acid could be obtained by treatment of ammonium sulphate in sulphuric acid solution with oxidising agents such as hydrogen peroxide, potassium chlorate, potassium persulphate, potassium permanganate, hydrated ferric oxide, potassium iodate, mercuric oxide, and mercuric chloride under the conditions prevailing in the earlier experiments of Browne and Shetterley on the oxidation of hydrazine. Ammonium sulphate in a solution strongly acidified with sulphuric acid is but slightly affected by prolonged treatment with such oxidising agents as hydrogen peroxide, potassium chlorate, and potassium permanganate at the boiling point. The addition of

ammonium sulphate to a reacting mixture of hydrazine sulphate, sulphuric acid, and hydrogen peroxide does not increase, but rather decreases the yield of azoimide obtained. Potassium nitrite oxidises hydrazine sulphate in sulphuric acid with formation under comparable conditions of larger yields of azoimide and of much smaller yields of ammonia than are obtained by the action of hydrogen peroxide on hydrazine sulphate. In view of the experimental results obtained and of various other considerations, the theory offered by Sommer (A., 1913, ii, 952) in explanation of the formation of azoimide and of ammonia by oxidation of hydrazine by means of oxidising agents which contain no oxygen is, in all probability, to be regarded as untenable. J. F. S.

Black Phosphorus. P. W. BRIDGMAN (*J. Amer. Chem. Soc.*, 1916, **38**, 609—612. Compare A., 1914, ii, 647).—The author has previously shown (*loc. cit.*) that white phosphorus, when heated at 200° at a pressure of 12,000 kilos, is converted into black phosphorus. The present paper deals with the formation of black phosphorus from red and violet phosphorus in the presence and absence of catalysts. When white phosphorus and red phosphorus with a trace of sodium are subjected to a pressure of 4000 kilos at room temperature and then heated at 200° at constant volume, there is a rise of pressure of 500 kilos. At 200° the pressure was then raised to 12,500 kilos for twenty minutes and then to 130,000 kilos for forty-five minutes. On cooling and releasing the pressure, it was found that the white phosphorus was entirely converted into violet phosphorus, but that the red phosphorus was unchanged. A piece of violet and a piece of red phosphorus in the presence of iodine were then subjected to a pressure of 8000 kilos at 20°, the temperature raised to 200° at constant volume, and the pressure then raised to 12,500 kilos for five and a half hours. No black phosphorus was formed, but the red phosphorus had been converted into violet phosphorus. All other attempts to convert red phosphorus into black phosphorus failed. An experiment was carried out on the rate of formation of black phosphorus from white phosphorus by measuring the rate at which the pressure changes. It is shown that at 200° and 12,000 kilos there is a slow fall in pressure for about fifteen minutes which amounts to 400 kilos, and then a sudden drop of pressure of 4000 kilos, after which, even though the pressure was brought to its original value, there was no further drop of pressure. This indicates that there is a period of preparation before the black phosphorus is formed suddenly. The experiments establish the facts (i) that black phosphorus is stable compared with white phosphorus at 200° at pressures above 4000 kilos; (ii) that violet phosphorus is stable compared with white phosphorus at 4000 kilos and somewhat below 200°; and (iii) that violet phosphorus is stable compared with red phosphorus at 200° between the pressures of 8000 and 12,000 kilos. J. F. S.

Action of Hydrogen Sulphide on Arsenic Acid. WILLIAM FOSTER (*J. Amer. Chem. Soc.*, 1916, **38**, 52—57).—The action of

hydrogen sulphide on solutions of arsenic acid in the presence of hydrochloric acid of various concentrations has been studied with the object of deciding between the discrepant results of Travers and Usher (T., 1905, **87**, 1370) and McCay (*Amer. Chem. J.*, 1887, **9**, 174). As the result of a large number of qualitative and quantitative experiments it is shown that arsenic acid is never reduced directly to arsenious acid and sulphur, but that when a solution of arsenious acid is treated with hydrogen sulphide the compounds react to form monosulphoxyarsenic acid, H_3AsO_3S. This substance is not very stable, and in the presence of dilute acids breaks down gradually into arsenious acid and sulphur. In the presence of concentrated acids the decomposition is much more rapid. Concentrated hydrochloric acid brings about the decomposition very rapidly, even at zero. A low concentration of hydrogen sulphide also favours the decomposition of this compound. These facts account for the presence of arsenic trisulphide and free sulphur in precipitates obtained by treating solutions of arsenic acid with hydrogen sulphide. When solutions of arsenic acid are treated with a rapid stream of hydrogen sulphide, no reduction takes place, even if no mineral acid is present. In an experiment it was observed that arsenic acid saturated with hydrogen sulphide yielded pure arsenic pentasulphide after the solution had stood for ninety-one hours. It was also found that no reduction occurred in solutions of arsenic acid in the presence of hydrochloric acid ranging in concentration from 0·9% to 32%, that is, when the solutions were treated at 15° with a rapid stream of hydrogen sulphide. These results are in complete agreement with those of McCay, but in most cases are at variance with those of Travers and Usher.

J. F. S.

[**Colloidal Arsenates.**] EUGEN DEISS (*Kolloid. Zeitsch.*, 1915, **16**, 16).—A claim for priority against Klemp and Gyulai (A., 1915, ii, 256) in respect of the preparation of manganous arsenate jellies. If a solution of potassium dihydrogen arsenate is used instead of trisodium arsenate, transparent jellies of manganous arsenate are obtained in the absence of both ammonium salts and acetic acid.

H. M. D.

Boric Acid Solutions in Presence of Litmus. FR. FICHTER (*J. Chim. phys.*, 1915, **13**, 399—401).—According to an observation of Rose (*Annalen*, 1852, **84**, 216), if a solution of litmus reddened by the addition of acid is added to a concentrated solution of borax until the red colour is very faint, the colour changes to blue when the solution is diluted. This has been attributed to increased hydrolysis of the sodium borate, but it is shown that the effect cannot be interpreted in this way, and is to be explained in terms of the ionisation of the boric acid which is set free by the acetic acid.

H. M. D.

The Problem of the Diamond. EMIL BAUR, K. SICHLING, and E. SCHENKER (*Zeitsch. anorg. Chem.*, 1915, **92**, 313—328).—Assum-

ing the value for the heat of transformation of diamond into graphite to be 180 cal. per gram-molecule at 17° (Roth and Wallach, A., 1913, ii, 384), and calculating by means of the formula of Nernst and Lindemann, the diamond is found to become less stable with increasing temperature. Assuming both phases to be incompressible, a pressure of 6250 atmospheres at 0° or of 44,000 atmospheres at 2000° would be necessary to convert graphite into diamond.

It appears, however, that the specific heats of the two modifications become almost equal at a red heat. Possibly the curves cross, and above 1000° absolute the specific heat of diamond is greater than that of graphite. The triple point under high pressures may be between 4000° and 5000° abs. Whatever assumptions may be made, the formation of diamond in the blast furnace, or in molten metal, must lie far outside any possible range of stability. The natural occurrence of diamond is opposed to its formation as an intermediate metastable phase.

When mixtures of iron and magnesium silicates, prepared by the thermit method, are mixed with calcium carbide and heated electrically, only graphite is obtained, even when the temperature is lowered to 1100—1200° by the addition of a flux.

Experiments under high pressures, using an apparatus capable of reaching 2000° under 10,000 kg./cm.^{2} by means of carbon resistance, using mixtures of silica and carbon, have also failed to give any form of carbon but graphite. Negative results are also obtained with silicates and carbides in the same apparatus (compare Threlfall, T., 1908, **93**, 1333). C. H. D.

Preparation and Properties of Colloidal Carbon. PERCY CYRIL LESLEY THORNE (T., 1916, **109**, 202—209).—Attempts to prepare a colloidal carbon by the dehydration of sucrose by sulphuric acid gave a sol containing a small amount of carbon, but its properties were obscured by the presence of complex decomposition products. A stable sol was obtained by passing an electric current (0·5—4·0 amperes at 200 volts) through dilute sodium hydroxide solution between carbon electrodes with the positive pole just touching the surface of the liquid. The sol showed a distinct Tyndall cone; in layers more than a few mm. thick it was black, and contained particles visible with the ultramicroscope. It was very sensitive to electrolytes, and analysis of the coagulum showed that it contained, in addition to an inorganic residue, considerable amounts of oxygen (19·05%) and hydrogen (2·35%). Organic matter is also formed in the sol, and its presence, as also that of a trace of alkali or some electrolyte, seems necessary to ensure the stability of the sol. G. F. M.

The Solidification of Silver–Arsenic Alloys. W. HEIKE and A. LEROUX (*Zeitsch. anorg. Chem.*, 1915, **92**, 119—126).—The investigation of this system by Friedrich and Leroux (A., 1906, ii, 283) is incomplete owing to the alloys having been prepared under atmospheric pressure. The alloys have now been prepared by fusion in sealed porcelain or siloxide tubes (Heike, A., 1913, ii,

477). The electric furnace is so mounted that the tube may be inverted to mix the metals. When the vapour pressure of the arsenic is high, the tube is enclosed in an outer porcelain vessel packed with sand.

The freezing-point curve shows a single eutectic point at 540° and 25 atomic % of arsenic. Solid solutions are only formed from 0 to 6 atomic %. Alloys between this composition and the eutectic undergo a transformation at 595°, whilst a second transformation at 374° is observed over almost the whole range of composition. The first is due to a reaction between the solid and liquid phases, forming a new solid solution with a limiting concentration of 10·5 atomic %, and the second to a eutectoid decomposition of the latter. Both changes may be suppressed by undercooling. The composition of the eutectoid is not indicated. Cold dilute sodium hydroxide is used for etching, but the eutectoid structure is best developed by means of potassium cyanide, and the same solution is used for alloys containing the two solid solutions, whilst undercooled alloys are best etched with warm sodium sulphide.

The freezing point of arsenic is found to be 814·5°±0·5.

C. H. D.

The Ternary System, $CaO-Al_2O_3-MgO$. G. A. RANKIN and H. E. MERWIN (*J. Amer. Chem. Soc.*, 1916, **38**, 568—588).—Concentration melting-point curves have been obtained for the binary systems: lime–magnesia, magnesia–alumina, and spinel–alumina. The melting point of magnesia has been found to be 2800°, and there is no indication of a second form existing. Alumina is found to exist in two forms: Al_2O_3 (α), artificial corundum, m. p. 2050°, and Al_2O_3 (β), a new form produced by melting alumina and allowing it to cool slowly. It has not been found possible to reconvert the β-form into the α-form after it has once been produced. β-Al_2O_3 is hexagonal, often appearing in groups of overlapping triangular plates with perfect basal cleavage. The composition–melting point diagram of Al_2O_3–CaO–MgO has been determined. Boundary curves and fields of existence are plotted and spatial diagrams given in the paper. The ternary system is of a simple character, since there are no ternary compounds stable in contact with the melt. The working out of the system therefore involved the equilibrium of the three components and the binary compounds $3CaO,Al_2O_3$, $5CaO,3Al_2O_3$, CaO,Al_2O_3, $3CaO,5Al_2O_3$, MgO,Al_2O_3 in ternary solutions. The whole of the relationships found to exist between the components and compounds in binary systems and in the ternary system are shown in a series of concentration–temperature diagrams. The optical and crystallographic properties of the components and pure compounds have been given in a previous paper (A., 1915, ii, 50), but a few new details are included in the present paper for $5CaO,3Al_2O_3$ and CaO,Al_2O_3. J. F. S.

Solid Solutions of Compounds of Calcium, Strontium, Barium, and Lead with those of the Rare Earths, and their Importance in Chemical Mineralogy. FERRUCCIO ZAMBONINI (*Reprint*, pp. 185, 1915).—The author has investigated, by thermal,

crystallographic, and microscopic methods, the formation of solid solutions between compounds of calcium, strontium, barium, and lead and the corresponding compounds of metals of the cerium and yttrium groups. The systems investigated and the results obtained are briefly as follows:

$BaCl_2$–$CeCl_3$ gives crystals of the type $BaCl_2,2H_2O$, containing up to 2·19% of cerous chloride. $Ca(NO_3)_2$–$Y(NO_3)_3$ forms crystals of the type $Ca(NO_3)_2,4H_2O$, containing up to 2·2% of hexahydrated yttrium nitrate. $Sr(NO_3)_2$–$Y(NO_3)_3$ gives crystals of the type $Sr(NO_3)_2$, with not more than 0·86% of yttrium nitrate, and crystals of the type $Sr(NO_3)_2,4H_2O$ with 1·8% of hexahydrated yttrium nitrate. $PbSO_4$–$Di_2(SO_4)_3$ and $BaSO_4$–$Di_2(SO_4)_3$, no miscibility. $PbMoO_4$–$Ce_2(MoO_4)_3$ forms mixed crystals containing up to 77—78% of cerous molybdate. The systems $PbMoO_4$–$La_2(MoO_4)_3$, $PbMoO_4$–$Di_2(MoO_4)_3$, $PbMoO_4$–$Pr_2(MoO_4)_3$, $PbMoO_4$–$Nd_2(MoO_4)_3$ and $PbWO_4$–$Ce_2(WO_4)_3$ show complete miscibility. $PbMoO_4$–$Y_2(MoO_4)_3$ forms mixed crystals containing up to 13·6% of the yttrium salt, and $CaMoO_4$–$Ce_2(MoO_4)_3$, mixed crystals containing up to 59·1% of cerous molybdate. $CaMoO_4$–$Di_2(MoO_4)_3$, mixed crystals containing 38·8% of the didymium salt. $CaMoO_4$–$La_2(MoO_4)_3$, mixed crystals containing up to 58% of the lanthanum salt. $CaMoO_4$–$Y_2(MoO_4)_3$, mixed crystals containing up to 4·7% of the yttrium salt. $CaMoO_4$–$Y_2(MoO_4)_3$–$Ce_2(MoO_4)_3$, mixed crystals containing 24·7% of the yttrium salt and 21% of the cerium salt. $SrMoO_4$–$Ce_2(MoO_4)_3$, mixed crystals containing 39·7% of the cerium salt. $SrMoO_4$–$La_2(MoO_4)_3$, mixed crystals with 37·5% of the lanthanum salt. $BaMoO_4$–$La_2(MoO_4)_3$, mixed crystals with 13·1% of the barium salt. $CaWO_4$–$Ce_2(WO_4)_3$, mixed crystals containing 10·3% of the cerous salt. $Pb_3(PO_4)_2$–$CePO_4$, mixed crystals of the type $Pb_3(PO_4)_2$ with 3% of cerous phosphate. $Pb_3(PO_4)_2$–$CeVO_4$, mixed crystals with 3·0% of cerous vanadate. $Ca_3(PO_4)_2$–$CePO_4$–$CaCl_2$, chloroapatite containing up to 13% of cerous phosphate. $Ca_3(PO_4)_2$–$DiPO_4$–$CaCl_2$, chloroapatite with 3%, and chlorospodiosite with 9%, of didymium phosphate. $Ca_3(PO_4)_2$–YPO_4–$CaCl_2$, chloroapatite with 6% of yttrium phosphate.

The molybdates and tungstates of the rare earth metals have molecular volumes about three times as great as those of the corresponding compounds of lead and calcium. It is evident that the view which is generally accepted, namely, that isomorphous compounds capable of giving an extended series of solid solutions possess similar molecular volumes, is erroneous. Confirmation of this conclusion is afforded by a number of other instances; thus, in the systems BaS–CaS and BaO–CaO the larger molecular volume is respectively 52·7% and 55·0% higher than the smaller one.

In the case of nickel and cobalt, the compounds of the metal with the higher atomic weight have the lower specific gravities, whereas with praseodymium and neodymium the reverse is the case.

Numerous crystallographic data are given for the mixed crystals obtained. The results given by the mixed molybdates and tungstates show that the magnitudes of the angles are not necessarily

a function of their composition, and need not lie between those of the pure components. Further, the values of $a:c$ for the molybdates of yttrium, lanthanum, cerium, praseodymium, and neodymium reveal no relation between the value of c and the atomic weight of the metal or the molecular volume of the salt (compare Jaeger, A., 1914, i, 797).

The above results are discussed in relation to the chemical composition of yttrofluorite, hellandite, eudialyte and eucolite, the minerals of the melanocerite group, knopite, and churchite.

T. H. P.

Solubility of Gypsum in Sea-water. A. MANUELLI (*Ann. Chim. Applicata*, 1916, **5**, 13—24).—Determinations have been made of the solubility of gypsum at 18° in sea-water from the Adriatic and in various mixtures of it with distilled water. The results show that an approximately fixed proportion of calcium sulphate is dissolved by sea-water and its aqueous solutions containing from 12 to 37 parts of saline residue per 1000; similar results were obtained with an artificial sea-water free from carbonates. In both cases the proportions of dissolved calcium sulphate calculated from the calcium oxide are greater than those calculated from the sulphur trioxide; the cause of this phenomenon has not been ascertained. It is evident that the constancy in the relations between the proportions of different salts in sea-water is due, not to the attainment of a condition of saturation with respect to certain salts, but to the enormous extent to which river waters are diluted in the whole mass of sea-water. T. H. P.

Density of Lead from Radioactive Minerals. THEODORE W. RICHARDS and CHARLES WADSWORTH, 3RD (*J. Amer. Chem. Soc.*, 1916, **38**, 221—227).—The density of ordinary lead, and of lead from radioactive minerals has been determined at 19·94° by weighing in a modified Ostwald-Sprengel pyknometer. It is shown that ordinary lead of atomic weight 207·2 has a density of 11·337, whereas lead from Australian radioactive sources of atomic weight 206·3 has a density of 11·288. The materials in both cases were purified by fractional crystallisation of the nitrate and chloride, and the subsequent treatment was identical in both cases. Continued fractionation of the radioactive lead had no effect on the density. The difference in density is particularly interesting, because it is practically parallel with the atomic weight, which indicates that radioactive lead and ordinary lead have the same atomic volume, the values being respectively 18·276 and 18·277. J. F. S.

Separation of the Rare Earths giving the more Soluble Double Sulphates from Brazilian Monazite Sand. C. JAMES and A. J. GRANT (*J. Amer. Chem. Soc.*, 1916, **38**, 41—47).—The material used in this investigation was the solution obtained after potassium sulphate had been added to the mixed rare earth sulphates in quantity insufficient to precipitate completely the whole of the cerium metals. The solution was precipitated by

oxalic acid, and the oxalates ignited to oxides. The mixture contained considerable quantities of lanthanum, cerium, praseodymium, and neodymium, in addition to samarium, gadolinium, and the yttrium earths. This mixture was first roughly fractionated as double magnesium nitrates in the following way: The mixed nitrates with magnesium nitrate in solution were evaporated until about one-half the material had crystallised on cooling. The crystals were twice recrystallised, and then placed on one side, the mother liquor being fractionated until the spectrum of samarium or erbium became intense. When this stage was reached the mother liquor was precipitated by oxalic acid and the oxalates ignited to oxides, this operation having the effect of removing large amounts of iron and aluminium. In this way three fractions were obtained: (*a*) The least soluble portion consisting of white or green crystals composed of lanthanum, cerium, and praseodymium magnesium nitrates with traces of the neodymium compound; (*b*) more soluble, deep amethyst crystals consisting mainly of neodymium magnesium nitrate with traces of the double magnesium nitrates of samarium, praseodymium, cerium, and lanthanum; (*c*) oxides from the mother liquor containing neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium, and lutecium. The cerium was removed from the fraction (*a*) by boiling the solution with potassium bromate and powdered marble (James and Pratt, A., 1911, ii, 935). A number of experimental details and precautions are described in connexion with this process. After the removal of the cerium, the solution was precipitated by oxalic acid, the oxalate ignited to oxides, and these converted into double ammonium nitrates and fractionated, whereby lanthanum and praseodymium were obtained. Neodymium was obtained pure by continuing the recrystallisation of (*b*). Fraction (*c*) was converted into double magnesium nitrates, and fractionally crystallised from 1 : 1 nitric acid, and whenever the mother liquor failed to crystallise properly a considerable quantity of magnesium bismuth nitrate was added. This rapidly removed the remaining europium and gadolinium. As soon as the mother liquors were free from gadolinium they were precipitated with oxalic acid. Continuing this fractionation for some time, five fractions were obtained: (i) crude neodymium magnesium nitrate, (ii) samarium magnesium nitrate, (iii) bismuth magnesium nitrate containing europium magnesium nitrate, (iv) gadolinium magnesium nitrate containing terbium, dysprosium, holmium, and small amounts of yttrium, and (v) oxalates, mainly yttrium, but containing dysprosium, holmium, erbium, thulium, ytterbium, lutecium, and traces of terbium. Gadolinium was obtained pure from fraction (iv) by conversion into oxalate, igniting to oxide and dissolving in bromic acid. The bromates were submitted to a long series of fractional crystallisations, when gadolinium was obtained at the less soluble end in a very pure condition. The fractions between gadolinium and dysprosium contained the terbium. Dysprosium and holmium were obtained from the bromate fractions more soluble than terbium, and from the yttrium earth oxides (*c*). Both materials

were converted into bromates and crystallised from water, when six fractions were obtained: (α) least soluble, dysprosium, holmium, and yttrium bromates containing traces of terbium; (β) yttrium bromate containing some dysprosium and holmium; (γ) yttrium bromate containing very small amounts of dysprosium, holmium, and erbium; (δ) yttrium bromate containing very small amounts of erbium; (ε) yttrium and erbium bromates; (ζ) bromates of erbium, thulium, ytterbium, lutecium, and celtium. The least soluble portions of the bromates were mixed, according to their compositions, with the corresponding fractions forming the more soluble end of the terbium gadolinium series and fractionated. After prolonged fractionation the terbium separated in the least soluble fractions, and the dysprosium was slowly removed from the holmium. The fractions (γ) and (δ) were mixed and worked up for yttrium by the four following methods: (i) the basic nitrate method, (ii) the nitrite method, (iii) the chromate method, and (iv) the cobalticyanide method. The basic nitrate and nitrite methods are the best for large quantities of material. The authors boiled a solution of nitrates of yttrium and erbium, and added sodium hydroxide until crystals of basic nitrate began to form. The liquid was then cooled, and the rose-coloured crystals, rich in erbium, removed. The process was then repeated with the filtrate. The precipitates become paler in colour as the yttrium is concentrated. The yttrium was further purified by boiling a dilute solution of the nitrate with sodium nitrite, which gave a very pure product. J. F. S.

Solution of the Cerium Group Oxides by Certain Acids. W. S. CHASE (*J. Ind. Eng. Chem.*, 1916, **8**, 239—240).—Oxides of the cerium group are fairly readily dissolved by sulphuric, hydrochloric, and nitric acids, but not by acetic acid. The addition of hydrogen peroxide accelerates the solution of the oxides in the mineral acids, even when the latter are diluted, and only a small excess of acid is required. Hydrogen peroxide does not, however, increase the solubility of the oxides in acetic acid. W. P. S.

Revision of the Atomic Weight of Neodymium. II. GREGORY PAUL BAXTER, WILLIAM HENRY WHITCOMB, OLUS JESSE STEWART, and HAROLD CANNING CHAPIN (*J. Amer. Chem. Soc.*, 1916, **38**, 302—310. Compare A., 1911, ii, 285).—Neodymium nitrate was purified by prolonged fractional crystallisation of the nitrate from concentrated nitric acid. The chloride was produced from this by conversion in oxalate, ignition, and solution in distilled hydrochloric acid. The chloride was then analysed by comparison with silver. The mean value of the atomic weight of neodymium is thus found to be 144·261. The average of this value and the value previously found by Baxter and Chapin (*loc. cit.*) is 144·268, so that the rounded figure Nd = 144·27 (Ag = 107·88) would seem to be the result of both sets of investigations. J. F. S.

Oxidation of Manganese Solutions in the Presence of Air. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1916, **38**, 638—640).—A

number of tubes were partly filled with a 1% solution of manganous chloride, and about 1 gram of calcite and one of the following substances were added: lead, bismuth, tin, arsenic, antimony, mercury, copper, zinc, nickel, cobalt, cadmium, silver, gold, mercuric sulphide, millerite, pyrites, chalcopyrite, and zinc blende. The tubes were sealed, and the time required for the production of hydrated manganese dioxide by the air oxidation noted. In a tube containing only the solution and calcite, the first noticeable separation took place after several weeks. Lead and bismuth accelerate the reaction, producing the same effect in a few hours. All the other substances had no accelerating effect. In fact, in the case of antimony, tin, and arsenic there was a retarding action, but this was due, not to a negative catalysis, but to the reducing action of the salts of these metals which would be formed. The bearing of the above action on the production of pyrolusite beds in nature is considered. J. F. S.

A Slag containing Manganese. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1915, **92**, 35—36).—A slag from a manganese furnace, of a brown colour, was found to contain manganese in ultra-microscopic particles, similar to those of gold in ruby glass. The particles have a golden lustre in the ultra-microscope.

It is not certain whether the manganese owes its origin to reduction of one of its compounds in the molten slag or to volatilisation of the metal and entrance of the vapour into the slag. The former mode of origin corresponds with that of ruby glass, and the latter with the origin of metal fogs. Experiments to produce a similar glass by melting manganese under a layer of glass have given negative results, although manganese vapour condenses to drops on the sides of the crucible. C. H. D.

Artificial Preparation, Fusibility, and other Properties of Silicates of the System $2FeO,SiO_2+2CaO,SiO_2$. B. SÉLIVANOV (*J. Soc. Chem. Ind.*, 1916, **35**, 307; from *Rev. Soc. Russe Métall.*, 1915, **11**, 328. Compare A., 1915, ii, 837).—Mixtures of pure silica, lime, and iron peroxide containing 60% FeO were melted in an iron crucible in a cryptol electric resistance furnace and cooling curves taken. The cooled product was in each case analysed, and from the results obtained the equilibrium diagram was constructed. Fe_2SiO_4 melts at about 1260° [?], and a maximum at about 1260° [?] corresponds with the compound $2Fe_2SiO_4,3Ca_2SiO_4$. Between these two points a eutectic point at 1160° corresponds with about 33% (molecular) Ca_2SiO_4. When the mixtures were heated in a current of hydrogen, reduction began at the following temperatures, corresponding with the annexed percentages of Fe_2SiO_4: 100%, 225°; 85%, 210°; 65%, 205—210°; 50%, 170°; 40%, 180°; and 30%, 250°. G. F. M.

Preparation of Pure Iron and Iron–Carbon Alloys. J. R. CAIN, E. SCHRAMM, and H. E. CLEAVES (*J. Ind. Eng. Chem.*, 1916, **8**, 217—223).—The iron was prepared electrolytically, and purified by fusion in magnesia crucibles; the magnesia used in making the

crucibles was prepared by converting magnesite into magnesium acetate and igniting the latter. The ingots obtained were sound and free from blow-holes. By fusing the pure iron with definite quantities of carbon in a magnesia crucible in a vacuum furnace, a series of iron–carbon alloys were prepared containing 99·96% of the two elements. W. P. S.

The Action of Sulphuric Acid on Alloy Steels. Leslie Aitchison (T., 1916, **109**, 288—298).—Fine drillings of the steels, passed through a sieve, are covered with 10% sulphuric acid and allowed to remain for a fixed time. After filtration, the solution is analysed, and the proportions of the two metals compared with those which would be found if the original ratio of the two metals in the steel had been preserved. The composition of the carbides in alloy steels is taken to be that determined by Arnold and Read (A., 1910, ii, 1971; 1911, ii, 1092; 1915, ii, 567).

Vanadium does not pass into solution until the steel contains 5·4% of the metal, showing that up to that point the whole of the vanadium is present in the carbide, which is not attacked by sulphuric acid under the conditions of the experiment. Chromium is present both in solid solution and also in the carbide, and the latter is slightly attacked. Alloys containing large percentages of chromium, however, give up very little to the acid. Tungsten is entirely present as carbide up to 11·5%, and this is not attacked by acid. Nickel, on the other hand, is present only in solid solution until high percentages are reached, whilst cobalt is contained only as carbide. Manganese is present both in solid solution and in the carbide, the latter being partly attacked owing to its fine state of division in the sorbitic pearlite. Double carbides are much less susceptible to attack by acid than pure iron carbide. C. H. D.

Crystals of Iron Phosphide from a Blast-furnace. L. J. Spencer (*Min. Mag.*, 1916, **17**, 340—343).—Small, tin-white needles with brilliant metallic lustre and strongly magnetic were found sparingly in drusy cavities, together with crystals of iron carbide and of metallic iron, in a large mass of metal from a blast-furnace near Middlesbrough. The crystals belong to the sphenoidal-hemihedral class of the tetragonal system, $a:c = 1:0·3469$. Their composition is presumably Fe_3P, and the material is identical, except in the absence of nickel, with the meteoric rhabdite. L. J. S.

The Formation of Isomorphous Mixed Crystals between Cobalt Oxide and Manganous Oxide, and between Cobalt Oxide and Nickel Oxide. J. Arvid Hedvall (*Zeitsch. anorg. Chem.*, 1915, **92**, 381—384 *).—When cobalt oxide and manganous oxide are heated together in a large excess of potassium chloride, solid solutions are obtained which vary continuously in colour with the composition. It is uncertain whether the miscibility is continuous or not.

Minute cubo-octahedra of nickelous oxide are obtained by

* and *Arkiv Kem. Min. Geol.*, 1916, **6**, No. 2, 1—5.

repeated heating of the amorphous oxide or hydroxide to 1000° in an excess of potassium chloride. They are light yellowish-green and have D 7·45.

Mixtures of cobaltous and nickelous oxides yield homogeneous octahedra and cubo-octahedra. The colour and specific volume vary continuously, indicating that complete miscibility probably occurs.

C. H. D.

The Reduction of Metallic Oxides with Hydrogen at High Pressures. EDGAR NEWBERY and JOHN NORMAN PRING (*Proc. Roy. Soc.*, 1916, [A], **92**, 276—285).—The effect produced by heating various metallic oxides at temperatures above 2000° in contact with hydrogen at a pressure of 150 atmospheres has been investigated in a specially designed apparatus consisting of a magnesia crucible heated by means of the current passing through a tungsten wire. The water vapour produced in the reaction was removed by metallic sodium.

Under these conditions chromic oxide and manganese dioxide are reduced to the corresponding metals. Prepared in this way, the metals are probably purer than those obtained by any of the methods used hitherto. The m. p. was quite sharp in both cases, the mean values, corrected to "black body" temperature, being 1230°±5° for manganese and 1615±15° for chromium. Other oxides examined were only partly reduced, vanadium pentoxide, columbium pentoxide, and titanium dioxide giving the corresponding monoxides, uranium oxide, U_3O_8, giving the dioxide UO_2, and cerium dioxide, CeO_2, giving the sesquioxide, Ce_2O_3.

Aluminium oxide, magnesium oxide, zirconium dioxide, yttrium oxide, and thorium dioxide were not reduced under the conditions of the experiment.

H. M. D.

Molybdenum Semipentoxide and its Salts. F. MAWROW and M. NIKOLOW (*Zeitsch. anorg. Chem.*, 1915, **92**, 135—144).—When the violet hypophosphomolybdenum compound (A., 1902, ii, 25, 144) is rubbed with ammonia, the yellowish-brown precipitate may be washed and dried, and is then sparingly soluble in water with a neutral reaction. It dissolves in acids, and may be reprecipitated by ammonia. If washed with dilute ammonia and then with absolute alcohol, the residue has the composition $NH_4Mo_2O_5,3H_2O$. On ignition in a current of carbon dioxide, the oxide, Mo_2O_5, is obtained.

The sodium compound, $NaMo_2O_5,3H_2O$, is obtained by treating the original violet compound with sodium hydroxide. It yields a dark violet substance, $NaMo_2O_5$, on heating. The corresponding barium compound, $BaMo_2O_5,3H_2O$, may also be obtained in the hydrated and anhydrous forms.

C. H. D.

Oxidation and Reduction without the Addition of Acid. II. The Reaction between Stannous Chloride and Potassium Dichromate. MARKS NEIDLE and JOSHUA C. WITT (*J. Amer. Chem. Soc.*, 1916, **38**, 47—52. Compare A., 1915, ii, 780).—The oxidation

of stannous chloride by potassium dichromate in the absence of acid has been studied. It is shown that the stoicheiometric relationships are the same as those obtaining in the presence of acid. When potassium dichromate is added in the theoretical quantity to a solution of stannous chloride in the absence of acid, brownish- and greenish-blue, gelatinous masses are formed, which dissolve and form a clear, deep olive-green solution when the whole of the dichromate has been added. These solutions appear red by transmitted light. The solutions were examined by dialysis and by extraction with alcohol, and are shown to consist of potassium and chromium chlorides, together with colloidal solutions of hydrated stannic and chromic hydroxides. On dialysis a clear sol, of the approximate composition $6SnO_2:1Cr_2O_3$, is obtained, and this sol contains the whole of the tin and about one-half of the chromium used in the reaction. The course of the reaction is given by the equation:

$$2K_2Cr_2O_7 + 6SnCl_2 + (6x + y)H_2O \rightleftharpoons 4KCl + 6SnO_2,xH_2O + Cr_2O_3,yH_2O + 2CrCl_3 + 2HCl.$$

J. F. S.

Hetero-poly-acids containing Vanadium. IV. Compounds containing Vanadic and Tungstic Acids. WILHELM PRANDTL and HANS HECHT (*Zeitsch. anorg. Chem.*, 1915, **92**, 198—212. Compare A., 1915, ii, 469).—A solution of tungstic acid in ammonia, acidified with acetic acid, at first contains a paratungstate, but passes in the course of a few months into the hexatungstate (metatungstate), from which hydrochloric acid does not precipitate tungsten, even on prolonged boiling. Solutions of alkaline vanadates also yield hexavanadates with a sufficient quantity of acetic acid; otherwise lower vanadates are obtained.

The following salts have been prepared by the action of acetic acid on solutions of mixed alkali tungstates and vanadates:

$Na_3V_3O_9,18NaHWO_4,36H_2O$, colourless crystals, losing vanadium on recrystallisation; $Na_4V_6O_{17},6NaHWO_4,32H_2O$ and $35H_2O$, yellowish-red; $K_4V_6O_{17},6KHWO_4,7H_2O$, yellowish-red;

$$(NH_4)_4V_6O_{17},4(NH_4)_2H_2W_3O_{11},6H_2O \text{ and } 8H_2O,$$

orange-red rhombohedra; $K_4V_6O_{17},4K_2H_2W_3O_{11},20H_2O$ and $18H_2O$; $Na_4V_6O_{17},4Na_2H_2W_3O_{11},38H_2O$ and $40H_2O$;

$$Ba_2V_6O_{17},4BaH_2W_3O_{11},30H_2O \text{ and } 35H_2O;$$

and also a series of known salts, which are now formulated as $M_2'H_2V_6O_{17},2M_3'H_3W_6O_{21},xH_2O$, all of which form deep red octahedra.

C. H. D.

Mineralogical Chemistry.

Review of the Processes of Chemical Transformation in Potash Deposits. M. Rósza (*Zeitsch. anorg. Chem.*, 1915, **92**, 297—300).—A summary of the results obtained in previous papers (A., 1914, ii, 376; 1915, ii, 355, 356, 473).—A purely thermal decomposition of carnallite into KCl and $MgCl_2,4H_2O$ can only

occur rarely, as the circulation of solution has the effect of preventing dehydration. The decomposition is actually hydrothermal.

C. H. D.

Proustite from Cobalt, Ontario. ARTHUR L. PARSONS (*Min. Mag.*, 1916, **17**, 309—313).—Analysis, by H. V. Ellsworth, of the small crystals, which were, however, imperfectly separated from impurities, gave:

Ag.	As.	S.	Sb.	Fe.	Co (+ trace of Ni).	Insol.	Total.
64·12	15·90	19·28	0·08	0·25	0·12	0·38	100·13

corresponding with proustite (Ag_3AsS_3), 94·62; pyrargyrite (Ag_3SbS_3), 3·77%; smaltite, 0·04%; pyrites, 0·05%; arsenic, 1·27%. A crystallographic description of the material is given, $a:c = 1:0·8015$, and a new crystal-form recorded.

L. J. S.

Crystallography and Dehydration of Torbernite. W. F. HALLIMOND (*Min. Mag.*, 1916, **17**, 326—339).—Torbernite is tetragonal with $a:c = 1:2·974$. Refractive index, 1·591. When the crystals lose water, owing either to rise in temperature to less than 100° or to being placed in a desiccator, there is a change to metatorbernite—a crystalline form with definite optical characters. This alteration is dependent, not only on the temperature, but also on the partial pressure of aqueous vapour in the surrounding space. Torbernite was kept over sulphuric acid of various strengths (corresponding with definite vapour pressures) and at various temperatures, and afterwards examined to ascertain if the change to metatorbernite had taken place; the points when plotted fall on one or other side of the transition curve of torbernite. The mineral is stable within very narrow limits.

L. J. S.

Natrolite from Kinbane, Co. Antrim. F. N. ASHCROFT (*Min. Mag.*, 1916, **17**, 305—308).—A description is given of the occurrence of fine specimens of delicate, acicular crystals of natrolite in basalt near Kinbane (White Head) on the north coast of County Antrim. Associated minerals are calcite and analcite. Analysis gave the following results, in close agreement with the formula $Na_2O,Al_2O_3,3SiO_2,2H_2O$:

SiO_2.	Al_2O_3 (+trace Fe_2O_3).	CaO.	Na_2O.	K_2O.	H_2O.	Total.
47·22	27·21	nil	15·86	0·06	9·70	100·05

L. J. S.

Chabazite from County Antrim. G. F. HERBERT SMITH; with topographical notes by F. N. ASHCROFT and chemical analyses by G. T. PRIOR (*Min. Mag.*, 1916, **17**, 274—304).—A detailed description is given of the occurrence and crystallographic characters of chabazite and the associated minerals (calcite, analcite, natrolite, and mesolite) found in the flows of basaltic lava at various localities in County Antrim. The crystals ($a:c = 1:1·0860$) are of the

gmelinite (hexagonal) or phacolite (rhombohedral) habit, and are usually twinned on the $c(111)$ or $r(100)$ planes, or on both. Refractive indices for sodium light, $\omega = 1{\cdot}490$, $\epsilon = 1{\cdot}480$. Analyses I—III are of crystals of the gmelinite habit from White Head at the entrance of Belfast Lough, IV of crystals of the phacolite habit from Craigahulliar, near Portrush, and V of phacolite from Killyflugh, near Ballymena:

	SiO_2.	Al_2O_3.	CaO.	SrO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	46·64	20·04	7·00	0·22	0·63	3·81	21·84	100·18	2·09
II.	46·75	19·79	8·25	0·23	0·33	2·17	22·09	99·61	2·07
III.	47·81	19·73	5·01	0·02	0·31	6·13	21·56	100·57	2·06
IV.	48·61	18·06	8·19	0·60	2·13	0·33	21·68	99·60	2·09
V.	48·82	18·53	8·81	0·26	1·20	0·37	22·09	100·08	2·09

The formulæ deduced from these analyses are respectively:

I.	$12\frac{1}{2}(CaAl_2Si_4O_{12},6H_2O)$	$+\ 7(Na_2Al_2Si_4O_{12},6H_2O)$	$+H_2O$.	
II.	15 ,,	$+\ 4$,,	$+1\frac{1}{2}SiO_2$	$+9H_2O$.
III.	9 ,,	$+10$,,	$+3SiO_2$	$+6H_2O$.
IV.	15 ,,	$+\ 3(K_2Al_2Si_4O_{12},6H_2O)$	$+8SiO_2$	$+12H_2O$.
V.	16 ,,	$+\ 2$,,	$+9SiO_2$	$+15H_2O$.

The amounts of silica and water in excess over that required for the usually accepted formula of chabazite, namely,

$$(Ca,K_2,Na_2)Al_2Si_4O_{12},6H_2O,$$

may be present in solid solution, as recently suggested by Foote and Bradley (A., 1911, ii, 122; 1912, ii, 568) in the case of nephelite and analcite. This formula may be written in the form

$$(Ca,Na_2,K_2)Al_2Si_2O_8,2H_2SiO_3,4H_2O\,;$$

here the first portion represents the lime-felspar ($CaAl_2Si_2O_8$) and nephelite ($Na_2Al_2Si_2O_8$) molecules, and these may be replaceable by the alkali-felspar molecule, $(Na,K)AlSi_3O_8$.

Gmelinite and phacolite are both identical with the species chabazite, differing only in crystal habit, and the difference in the amount of soda and potash shown in the above analyses is probably without significance. L. J. S.

Gay Gulch and Skookum Meteorites, Yukon, Canada. R. A. A. Johnston (*Museum Bull.*, No. 15 [*Geol. Ser.*, No. 26]; *Geol. Survey Canada*, 1915, 1—31).—These masses of meteoric iron were found in the gold-bearing gravels of Pliocene age in two of the gulches tributary to the Bonanza Creek in the Klondike district, the second of them at a depth of 65 feet below the surface. One weighing 483 grams was found in 1901 in Gay gulch (partial analysis I by H. A. Leverin), and the other, weighing 15·88 kilograms, was found in 1905 in Skookum gulch (anal. II). They are both nickel-rich irons showing a similarity in structure (coarse octahedral with chatoyant reflections on the etched surfaces, nodules of troilite, etc.), and they probably belong to the same meteoritic shower dating back to the Tertiary period.

	Fe.	Ni.	Co.	Cr.	C.	P.	S.	Si.	Total.	Sp. gr.
I.	83·85	15·03	—	—	—	—	—	—	—	7·566
II.	80·65	18·20	0·91	0·002	0·015	0·194	0·002	0·003	99·976	7·561

L. J. S.

Summation of Chemical Analyses of Rocks. H. H. ROBINSON (*Amer. J. Sci.*, 1916, [iv], **41**, 257—275).—Although the sum of the results obtained in the complete analysis of a rock should be 100%, such is rarely the case. Inspection of the 3391 analyses recorded by Washington (*Bull. U.S. Geol. Survey*, Nos. 14 and 28, 1903, 1904) shows that the sum is more frequently above 100 than below; in 1253 cases the sum varied from 99% to 99·99%, and in 1846 it lay between 100 and 100·99%. The author discusses the question in general, showing that the errors are usually due to want of skill on the part of the analyst, and not particularly to the untrustworthiness of the methods employed. W. P. S.

Analytical Chemistry.

Action of Neutral Salts on Indicators. I. M. KOLTHOFF (*Chem. Weekblad*, 1916, **13**, 284—297).—Experiments on the effect produced by neutral salts on the colour of indicators show that the phenomenon is dependent on change in the concentration both of the hydrogen ions and the hydroxyl ions. A. J. W.

Succinic Acid as a Standard. C. A. PETERS and V. SAUCHELLI (*Amer. J. Sci.*, 1916, [iv], **41**, 244—248).—Results obtained by standardising ammonia solution against hydrochloric acid agreed closely with those found by the use of succinic acid electro-titrametrically, as described by van Suchtelen and Itano (A., 1914, ii, 775), but no trustworthy values could be obtained by the action of succinic acid on ammonia, using cochineal as indicator, as described by Phelps and Hubbard (A., 1907, ii, 297). W. P. S.

Use of Copper Oxide for Fractional Combustion of Hydrogen and Carbon Monoxide in Gas Mixtures. G. A. BURRELL and G. G. OBERFELL (*J. Ind. Eng. Chem.*, 1916, **8**, 228—231).—The copper oxide method devised by Jäger (compare A., 1909, ii, 698) for the fractional combustion of hydrogen and carbon monoxide yields trustworthy results. A temperature of the copper oxide of between 275° and 300° is adapted for burning hydrogen and carbon monoxide in a wide variety of gas mixtures. W. P. S.

Electrolytic Estimation of Iodine Present in Organic Matter. ROBERT B. KRAUSS (*J. Biol. Chem.*, 1916, **24**, 321—325. Compare A., 1915, ii, 791).—The results obtained by the palladous iodide colorimetric method may be checked by first depositing the palladium on a weighed platinum cathode and then the iodine on a silver-plated anode. The method is far less sensitive than the colorimetric estimation. H. W. B.

Decomposition of Tetrathionates in Alkaline Solution as a Source of Error in Certain Iodine Titrations. ROBERT M. CHAPIN (*J. Amer. Chem. Soc.*, 1916, **38**, 625—626).—When sodium tetrathionate, produced in iodine titrations, is allowed to remain in the presence of alkalis or alkaline salts, it is partly converted into sodium thiosulphate and sodium sulphite, thus introducing the possibility of an error in the estimations. The effect of allowing sodium hydroxide, sodium carbonate, ammonia, and sodium hydrogen carbonate to act on sodium tetrathionate solutions for fifteen minutes at 30° has been determined by titration with iodine. It is shown that with the exception of sodium hydrogen carbonate the conversion has taken place to a considerable extent. It therefore follows that acid solutions containing tetrathionates, if later to be titrated with iodine or subjected to any treatment involving the assumption that the tetrathionate present has remained unaffected, should never be neutralised by any substance of distinctly alkaline properties. In the case of arsenic estimations it seems safer to abandon the use of sodium thiosulphate and to substitute a dilute solution (0·5%) of sodium sulphite. J. F. S.

Differential Iodometry. I. Estimation of Periodates, Iodates, Bromates, and Chlorates in the Presence of each other. O. L. BARNEBEY (*J. Amer. Chem. Soc.*, 1916, **38**, 330—341).—The conditions under which the above-mentioned substances can be estimated in the presence of one another have been studied experimentally. It is shown that by careful regulation of the temperature, concentration of the agents, and especially of the acidity and the time of reaction, all these substances can be estimated iodometrically either alone or in the presence of one another. When periodates are treated with potassium iodide in a saturated solution of boric acid containing sufficient borax to diminish slightly the acidity, a reduction occurs to iodate with the liberation of iodine. Iodates are acted on by 0·1*N*-potassium iodide in 0·25*N*-acetic acid solution, liberating iodine. In 0·2*N*-hydrochloric acid solution containing 0·1*N*-potassium iodide, bromates are completely decomposed, liberating iodine. In 6*N*-hydrochloric acid solution of 0·1—0·2*N*-potassium iodide chlorates are completely decomposed, liberating iodine, and in this case, after rendering the solution alkaline and then acidifying, the iodine may be titrated by thiosulphate solution. By combining the above reactions, the whole of these substances can be estimated in the presence of one another and in the presence of perchlorates, which do not react readily with potassium iodide in acid solution. A number of test analyses are given in the paper which show that the method is trustworthy. J. F. S.

Reagents for Use in Gas Analysis. II. Chromous Chloride. R. P. ANDERSON and J. RIFFE (*J. Ind. Eng. Chem.*, 1916, **8**, 24—26. Compare A., 1915, ii, 647).—Chromous chloride has been proposed for the absorption of oxygen, but the authors find that it is not a very trustworthy reagent. If prepared by treating

chromous acetate with hydrochloric acid, the solution is not stable, hydrogen being evolved gradually. By reducing violet chromic chloride with hydrogen and filtering the solution through glass-wool (to remove insoluble substances, possibly metallic chromium), a stable solution of the reagent is obtained, but this does not absorb oxygen completely. W. P. S.

Reagent for Use in Gas Analysis. III. The Specific Absorption of Alkaline Pyrogallol in Various Pipettes. R. P. Anderson (*J. Ind. Eng. Chem.*, 1916, **8**, 131—133. Compare A., 1915, ii, 647).—Experiments with the Orsat pipette and modifications of the same described by Hankus, Nowicki, and Dennis (A., 1913, ii, 424) showed that, as regards time consumed in manipulation and the specific absorption obtained, the Orsat pipette is superior to any of the others when modified pyrogallol reagent (*loc. cit.*) is used for the absorption. The reagent is not, however, well suited for use in pipettes which have been designed for the absorption of oxygen without shaking (see following abstract). W. P. S.

Pipettes Specially Adapted for Use with Alkaline Pyrogallol. R. P. Anderson (*J. Ind. Eng. Chem.*, 1916, **8**, 133—135).—Two modifications of the Orsat pipette are described. In one, a perforated porcelain cone supports the glass tubes, and any precipitate which may form cannot collect and clog the lower ends of the tubes. The other form is similar to a Hempel double pipette, but the cylindrical portion is smaller than usual and is filled with glass tubes, the construction of the lower part of the cylinder being such that the tubes are held in position and do not become clogged with precipitate. The reagent used in the pipettes contains 21·2 grams of pyrogallol and 66·6 grams of potassium hydroxide per 100 c.c. The specific absorption (compare A., 1915, ii, 647) of this reagent for one minute contact is about 36 when treated in the above pipettes at 20° with gas samples 100 c.c. in volume and containing 20·9% of oxygen. W. P. S.

Reagents for Use in Gas Analysis. IV. Phosphorus in Solution. R. P. Anderson and W. Biederman (*J. Ind. Eng. Chem.*, 1916, **8**, 135—136).—The solution of phosphorus in castor oil proposed by Centnerszwer (A., 1910, ii, 541) is not suitable for the estimation of oxygen, the absorption of the gas being incomplete at the ordinary temperature. Even assuming that complete absorption can be attained by heating the reagent, there appears to be no reason why the latter should be preferred to alkaline pyrogallol properly prepared (compare A., 1915, ii, 647). W. P. S.

Methods for the Analysis of Lime-Sulphur Solutions. Robert M. Chapin (*J. Ind. Eng. Chem.*, 1916, **8**, 151—156).—Methods are described for estimating the concentration of total (sulphide) base, total (sulphide) acid, and excess of acid or base. The sulphide base number is represented by the c.c. of $N/10$-acid

solution required to neutralise 10 c.c. of the sample, using methyl-orange or Congo-red as indicator; in the case of lime–sulphur solutions which have already been used for dipping sheep, sodium nitroprusside may be used as an external indicator. The reaction number depends on the fact that sodium tetrathionate reacts with lime–sulphur solution to yield a solution which can be titrated in the usual way, the result giving the acidity or alkalinity of the sample; the reaction proceeds normally only in a dilute ammoniacal solution. The sulphide acid number is the difference between the base and reaction numbers, or it may be estimated iodometrically in the solution resulting from the estimation of the reaction number; alternatively, it may be found by titrating an ammoniacal solution of the sample with tetrathionate solution, nickel sulphate being used as the indicator. W. P. S.

Rapid Control Method for the Estimation of Sulphur in Pyrites Cinder. H. C. MOORE (*J. Ind. Eng. Chem.*, 1916, **8**, 26—28).—The sodium peroxide fusion method is recommended. About 1·5 gram of the finely powdered sample is fused in a wrought-iron or nickel crucible with 7 grams of sodium peroxide, the cooled mass is dissolved in water, and slightly acidified with hydrochloric acid. About 0·5 gram of aluminium powder is now added, and, when the ferric salts have been reduced, the solution is heated to boiling, cooled, diluted to 500 c.c., and filtered. Two hundred c.c. of the filtrate are diluted to 450 c.c., 1 c.c. of concentrated hydrochloric acid is added, and the sulphuric acid is precipitated by treating the cold solution with barium chloride solution. After one hour, the barium sulphate is collected, washed with cold water, ignited, and weighed. The presence of considerable quantities of barium sulphate and silica in the cinder does not have an appreciable influence on the results obtained. W. P. S.

Estimation of Sulphur in Spent Oxide. E. V. ESPENHAHN (*J. Soc. Chem. Ind.*, 1916, **35**, 292—293).—Sulphur in the spent oxide of the gas works may be accurately estimated by heating 0·4—0·7 gram of the finely powdered and washed material with 4 grams of reduced iron in a hard-glass crucible, whereby it is completely converted, after seven to ten minutes at a dull red heat, into ferrous sulphide. After cooling in an atmosphere of carbon dioxide, it is decomposed in a conical flask with concentrated hydrochloric acid, and the evolved hydrogen sulphide is passed into $N/10$-iodine and titrated in the usual way. The carbon disulphide extract of the spent oxide gives the sulphur and tar, whence by difference the tar content is obtained. The estimation of total sulphur, including that combined as sulphates and thiocyanates, is carried out by heating the powdered, but unwashed, oxide with iron as above, these salts being thereby likewise converted into ferrous sulphide, which is estimated by decomposing with hydrochloric acid as above described. G. F. M.

Estimation of Sulphur Dioxide and Sulphur Trioxide in Flue Gases. R. J. NESTELL and E. ANDERSON (*J. Ind. Eng. Chem.*, 1916, **8**, 258—260).—A definite volume of the flue gas (say,

2000 c.c.) is aspirated through the following series of absorption vessels: A U-tube containing a small quantity of water, a double filter-paper held between the large ends of two funnels, and a flask containing $N/10$-sodium carbonate solution and hydrogen peroxide; a glass tube, 3 feet long, conducts the gases from the flue to the apparatus. After the tube has been withdrawn from the flue, 1000 c.c. of air are drawn through the apparatus. The sulphur trioxide is retained, in the form of sulphuric acid, in the glass tube, the U-tube containing water and by the filter-paper. The latter, together with the rinsings of the tube and the solution in the U-tube, is placed in a flask and titrated with standard alkali solution to obtain the quantity of sulphur trioxide present. The sulphur dioxide passes entirely into the sodium carbonate solution, where it is absorbed and at the same time oxidised by the hydrogen peroxide; titration of the excess of sodium carbonate gives the amount of the sulphur dioxide in the flue gas. W. P. S.

A New Method for the Iodometric Estimation of Thiocyanic Acid and Hydrogen Sulphide. F. P. TREADWELL and C. MAYR (*Zeitsch. anorg. Chem.*, 1915, **92**, 127—134).—The iodometric method for the estimation of thiocyanates by Thiel (A., 1902, ii, 706) is tedious, and there is danger of loss of iodine in the evolution of carbon dioxide. If nascent bromine is used instead of iodine for the oxidation, the titration may be carried out quite rapidly. The solution is diluted until about $N/5$ or $N/6$, and 5 or 10 c.c. are introduced into a litre flask provided with a tap funnel, and 50 c.c. of $N/5$-potassium bromate and 10—15 c.c. of a 10% solution of potassium bromide are added. The flask is then evacuated with a filter pump, and sufficient concentrated hydrochloric acid is allowed to enter, without admitting air, until the volume of liquid is increased by one-third. After shaking, the flask is allowed to remain for fifteen minutes, when a solution of 2 or 3 grams of potassium iodide is added without admitting air. After again shaking, the separated iodine is titrated with $N/10$-sodium thiosulphate and starch.

Thiocyanates and chlorides or bromides may be estimated together by proceeding as above, and also by titrating thiocyanate and haloid together by Volhard's method.

The estimation of hydrogen sulphide by means of bromide and bromate is more exact than that by means of iodine, the reactions being $H_2S + 4H_2O + 8Br = 8HBr + H_2SO_4$ and $H_2S + I_2 = 2HI + S$. When concentrated hydrochloric acid is added, the solution at first becomes turbid from precipitation of sulphur, but this is oxidised in fifteen to twenty minutes, and the liquid becomes clear. In very dilute solutions thirty minutes may be required.

When sulphides and thiocyanates are both present, the sulphide sulphur is first estimated by the ordinary iodometric method, and then the total sulphur by the bromide–bromate method. Analyses are given to show the accuracy of the methods. C. H. D.

Quantitative Micro-elementary Analysis of Organic Substances. J. V. Dubsky (*Chem. Zeit.*, 1916, **40**, 201—203. Compare A., 1914, ii, 485).—Certain modifications are introduced into the methods described previously by the author (*loc. cit.*). The supply of carbon dioxide in the estimation of nitrogen by the micro-Dumas method is obtained from a small tube containing sodium hydrogen carbonate; the closed end of this tube is surrounded by wire gauze, which is heated by a burner, and the delivery tube is provided with a wash-bulb containing a few drops of water. In the estimation of carbon and hydrogen there is no need to use a diffusion-stopper in the combustion tube after the platinum boat containing the substance. Capillaries filled with calcium chloride and soda-lime respectively are used for the absorption of the water and carbon dioxide. W. P. S.

Kjeldahl Method for Estimating Nitrogen. I. K. Phelps and H. W. Daudt (*Proc. Amer. Soc. Biol. Chem.*, 1915; *J. Biol. Chem.*, 1916, **24**, xxxv.).—The quantity of nitrogen in members of the following classes of cyclic compounds, namely, pyrrole, pyrrolidine, pyridine, piperidine, quinoline, *iso*quinoline, purine, glyoxaline, quinoxaline, and quinazolone, can be estimated accurately by the Kjeldahl method provided the digestion is carried on for two and a-half hours with a boiling mixture of 25 c.c. of concentrated sulphuric acid, 10 grams of potassium sulphate, and 0·7 gram of mercuric oxide to 0·3 gram of the nitrogenous substance.

H. W. B.

Comparison of Methods for the Estimation of Soil Phosphorus. W. O. Robinson (*J. Ind. Eng. Chem.*, 1916, **8**, 148—151).—The fusion methods (with sodium carbonate, magnesium nitrate, etc.), Washington's method (decomposition with hydrofluoric and nitric acids), and Fisher's method (two evaporations with aqua regia with an intervening ignition), of treating soils for the estimation of phosphorus all give trustworthy results. Vanadium (always present in soils) interferes with the estimation, but its influence may be eliminated by the procedure described by Cain and Tucker (A., 1913, ii, 875); tungsten and titanium do not interfere. The insoluble precipitate sometimes obtained when the phosphomolybdate precipitate is dissolved in ammonia is probably due to the presence of iron, aluminium, titanium, etc., which have not been removed by proper washing. W. P. S.

New Method for Citrate-insoluble Phosphoric Acid. Chas. H. Hunt (*J. Ind. Eng. Chem.*, 1916, **8**, 251—253).—In the proposed method the sample is dissolved as for the estimation of total phosphoric acid, and the solution is diluted to a definite volume. An aliquot portion of the solution is then treated with an excess of ammonia, the precipitate formed is collected, washed, dissolved in nitric acid, and the phosphoric acid is estimated in this solution. The ratio between the citrate-insoluble P_2O_5 and the P_2O_5 precipitated by ammonia is approximately as 1:1·5; if, therefore, the

amount of P_2O_5 precipitated by ammonia is divided by 1·5, the quantity of citrate-insoluble P_2O_5 is found. The results obtained by the method agree well with those obtained by the usual (official) process. W. P. S.

Estimation of Phosphoric Acid Soluble in Citric Acid in Basic Slag by the Iron Citrate Method. M. POPP (*Chem. Zeit.*, 1916, **40**, 257—260. Compare A., 1912, ii, 992; 1913, ii, 336, 876; 1914, ii, 576).—Although ferric chloride varies considerably in composition (samples examined by the author containing from 58·8% to 99·6% of actual ferric chloride), the iron–citrate solution used to prevent the interference of silica always contains a quantity of iron sufficient for this purpose, even when the solution is prepared from ferric chloride of poor quality. The hydrogen peroxide solution used in the estimation maintains its strength for a considerable time if 0·005% of acetanilide is added; the presence of 0·5% of alcohol also preserves the strength of the solution. The quantity of hydrogen peroxide solution added should be from 1 to 3 c.c.; larger quantities cause the results obtained to be too low. This is not the case when dealing with pure phosphate solutions mixed with manganese and calcium salts, but the error always occurs with basic slag, and is evidently due to some constituent of the latter (possibly silica). W. P. S.

Officinal Sodium Sulphate. P. CARLES (*J. Pharm. Chim.*, 1916, [vii], **13**, 219—221).—Arsenic is liable to be present in certain samples of sodium sulphate, and the author suggests a modification of Marsh's test for detecting its presence. The issuing gas from the hydrogen generator is passed on to a paper moistened with a solution of mercuric chloride, and after the purity of the hydrogen has been ascertained about 25 grams of the salt under examination are placed in the hydrogen generating apparatus. The formation of a yellow or brown stain on the paper indicates the presence of arsenic, the depth of the colour giving an approximate measure of the amount present. W. G.

A New Method for the Detection and Qualitative Separation of Arsenic, Antimony, and Tin. FRIEDRICH L. HAHN (*Zeitsch. anorg. Chem.*, 1915, **92**, 168—170).—On account of the difficulty of the usual method of separation of these metals, the following modification is proposed: The mixture of sulphides and sulphur obtained in the usual way by the addition of acid to the solution in yellow ammonium sulphide is extracted with a cold 5% solution of sodium sulphide. The metallic sulphides dissolve readily, whilst the sulphur remains as a powdery residue. After filtration, the filtrate is made alkaline with sodium hydroxide, about twice as much of a 10% solution being added as was used of sodium sulphide. Hydrogen peroxide is then added, and the solution is heated to boiling. The evolution of oxygen shows that sufficient has been added.

Should antimony be present, it soon separates as glistening

crystals of $Na_2H_2Sb_2O_7$, which cling to the glass where rubbed. To complete the precipitation, one-fourth of the volume of alcohol is added. After filtration, the alcohol is expelled by boiling, and ammonium nitrate is added as a solid or as a concentrated solution. Stannic acid is precipitated, the separation being complete when the ammonia has been boiled off. Arsenic is precipitated from the filtrate as ammonium magnesium arsenate. The arsenic and antimony precipitates are very characteristic; the tin may be confirmed by dissolving in hydrochloric acid and adding mercuric chloride in the usual way. One mg. of arsenic, antimony, and 2 mg. of tin may be detected in 1 gram of copper or lead.

Should it be known that mercury is absent, the hydrogen sulphide precipitate may be treated directly with sodium sulphide solution, more sodium hydroxide and hydrogen peroxide being then necessary to oxidise the sulphur to sulphate, much heat being developed.

C. H. D.

Simultaneous Estimation of Carbon and Halogen by the Chromic Acid Method. PHILIP WILFRED ROBERTSON (T., 1916, **109**, 215—221).—Carbon and halogen may be simultaneously estimated in organic compounds by the chromic acid oxidation method previously described (T., 1915, **107**, 902). The substance is gently heated with a mixture of chromic and sulphuric acids, and the evolved gases are carried along by a slow stream of oxygen through a heated silica tube containing platinised asbestos, a **U**-tube containing glass-wool moistened with sulphuric and chromic acids to retain oxides of sulphur, and a second heated silica tube (in the case of chloro-compounds) to decompose chromyl chloride, into two absorption tubes, the first containing 10 c.c. of 1·3*N*-sodium hydroxide and 2 c.c. of 2*N*-sodium sulphite, and the second 10 c.c. of sodium hydroxide. The operation is complete in about one and a-half hours, and the mixed contents of the absorption tubes are then treated with 5 c.c. of hot barium nitrate solution, and after filtration the alkali in the filtrate is titrated with *N*/3-nitric acid with phenolphthalein as indicator. The difference between this titration and the blank gives the carbon dioxide and halogen, and the latter is then separately estimated in the same solution by adding an excess of silver nitrate and nitric acid, and titrating back with ammonium thiocyanate.

G. F. M.

Estimation of Carbon in the Organic Non-sugar Constituent of Saturation (Sugar) Scums. VL. STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1916, **40**, 201—206).—The carbon is estimated by oxidation with chromic acid–sulphuric acid solution. From 1 to 2 grams of the material are placed in a small flask provided with a glass stopper, which carries a tapped funnel and a condenser. Ten c.c. of 0·5% alkali hydroxide solution are added, and then 5 grams of crystallised phosphoric acid; the mixture is boiled gently to expel carbon dioxide, cooled, 5 grams of chromic acid are added, and the upper end of the condenser is connected with a combustion tube containing copper oxide and two pieces of silver gauze; this tube is

heated in a suitable furnace. Concentrated sulphuric acid is now admitted to the flask from the tapped funnel and the mixture is boiled; the condenser prevents steam from passing into the combustion tube. The gases leaving the latter are passed through a tube containing chromic acid, then dried, and the carbon dioxide is absorbed in a soda–lime tube. A current of air free from carbon dioxide is passed through the apparatus when the oxidation has been completed. The sugar content of the sample is estimated in a separate portion, and the quantity of carbon dioxide due to sugar is deducted from the total amount of carbon dioxide found.

W. P. S.

Rapid Method for the Estimation of Carbon Dioxide. W. H. WAGGAMAN (*J. Ind. Eng. Chem.*, 1916, **8**, 41).—The carbonate is decomposed in a conical flask, the upper part of which is surrounded by a cooling coil. The delivery tube of the flask is connected with a short, inclined condenser, and the other end of the latter is connected with the following series of absorption vessels: A U-tube containing silver sulphate solution (to retain hydrochloric acid), a sulphuric acid bulb, potash bulbs, a calcium chloride tube, a sulphuric acid bulb, and a tube containing barium hydroxide solution. The latter indicates any loss of carbon dioxide due to too rapid passage of the gas through the absorption bulbs, and also shows when the potash bulb has become exhausted. A current of air is drawn through the apparatus, the air being passed previously through potassium hydroxide solution contained in a flask; this flask also carries an Ostwald regulator, by means of which the supply of gas to the burner under the decomposition flask is regulated. The apparatus may be used for the estimation of carbon dioxide in soils, organic substances, etc. W. P. S.

Estimation of the Carbon Dioxide Tension in the Alveolar Air. W. McK. MARRIOTT (*Proc. Amer. Soc. Biol. Chem.*, 1915, xviii.; *J. Biol. Chem.*, 1916, **24**).—The carbon dioxide tension in the sample of air is estimated by bubbling the air through a 0·01*N*-solution of sodium hydrogen carbonate containing phenolsulphonephthalein as an indicator. The reaction of the solution and the corresponding colour obtained are functions of the carbon dioxide tension. The colour is compared with that of standard solutions of mixed phosphates containing the indicator made up in such a way that the tension of carbon dioxide in mm. may be directly read off. Changes in the barometric pressure and slight changes in temperature are without effect on the accuracy of the method. The results agree closely with those afforded by Haldane's method. H. W. B.

Method of Gas Analysis. O. A. KRONE (*J. Ind. Eng. Chem.*, 1916, **8**, 231—237).—A detailed description is given of a method and apparatus for the analysis of gas mixtures containing carbon dioxide, illuminants, oxygen, carbon monoxide, methane, ethane, hydrogen, and nitrogen. For concentrations of oxygen not exceed-

ing 5%, phosphorus is used to separate this gas; for higher concentrations, and when carbon dioxide and carbon monoxide are not present, the use of copper in the presence of ammoniacal ammonium chloride solution is recommended for the purpose.

W. P. S.

Rapid Method of Estimating Alkali in Potable Water. M. WAGENAAR (*Pharm. Weekblad*, 1916, **53**, 232—238).—A modified form of the barium hydroxide method for estimating the alkali metals in water.

A. J. W.

A Colorimetric Method Used by the Romans to Characterise Soft Waters. A. TRILLAT (*Compt. rend.*, 1916, **162**, 486—488).—The method of the Greeks and Romans (compare Hippocrates, "Traité des Airs, des Eaux et des Lieux," Chap. 36) for detecting the presence of alkalis in natural waters by the decoloration of red wine can be made to give an approximate measure of the hardness of different waters. The degree of hardness is indicated by the number of drops of red wine required to produce a coloration in the water as compared against a standard water. W. G.

Rapid Method for the Analysis of Limestone for Agricultural Purposes. A. S. BEHRMAN (*J. Ind. Eng. Chem.*, 1916, **8**, 42—43).—One gram of the powdered limestone is mixed with 50 c.c. of $N/2$-hydrochloric acid and a few drops of 3% hydrogen peroxide solution, and heated at 86° for thirty minutes. The mixture is then cooled, 5 grams of ammonium chloride and some macerated filter-paper are added, followed by 25 c.c. of $N/2$-ammonia solution. After fifteen minutes the precipitate, etc., is collected on a filter, washed with 10% ammonium nitrate solution, ignited, and weighed; the weight gives the quantity of insoluble substances, ferric hydroxide, and aluminium hydroxide present. The filtrate is titrated with $N/2$-hydrochloric acid, using methyl-orange as indicator. The total carbonates are found by subtracting the weight of the precipitate from 100, and the amount of hydrochloric acid required for the decomposition is a measure of the carbon dioxide in the carbonates; the actual quantities of calcium and magnesium carbonates in the sample may be calculated from these data. The results obtained by the method are only approximately correct, the error being about 2% or 3%.

W. P. S.

Micro-colorimetric Estimation of Calcium and of Inorganic Phosphates in the Blood Serum. JOHN HOWLAND, F. H. HAESSLER, and W. McK. MARRIOTT (*Proc. Amer. Soc. Biol. Chem.*, 1915, xviii.–xix.; *J. Biol. Chem.*, 1916, **24**).—The methods described are based on the fact that the red colour of a solution of ferric thiocyanate is discharged by certain substances, among which are oxalates and phosphates.

Calcium is precipitated as oxalate, dissolved in acid, added to a standard solution of ferric thiocyanate, and made up to a definite

volume. The colour of the resulting solution is compared with that of a solution containing known amounts of calcium oxalate and ferric thiocyanate. The phosphates are precipitated as magnesium ammonium phosphate; the precipitate is then dissolved in acid, added to ferric thiocyanate solution, and colour comparisons made as above.

The calcium content of the serum in children is not diminished in cases of rickets except when accompanied by tetany. Parathyroidectomy in dogs is followed by a progressive diminution in the calcium content of the serum. H. W. B.

Estimation of Calcium in Blood. JOHN O. HALVERSON and OLAF BERGEIM (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxii.; *J. Biol. Chem.*, 1916, **24**).—Ten c.c. of blood are deproteinised by means of picric acid, and the calcium in the filtrate precipitated as oxalate. The precipitate is washed by centrifugal action and the oxalate titrated with 0·01*N*-permanganate solution.

Magnesium is estimated in the filtrate by precipitation as magnesium ammonium phosphate, the ammonia content of which is estimated after distillation colorimetrically or by direct titration. H. W. B.

Solubilities of the Sulphates of Barium, Strontium, Calcium, and Lead in Ammonium Acetate Solutions at 25°, and a Criticism of the Present Methods for the Separation of these Substances by means of Ammonium Acetate Solutions. J. W. MARDEN (*J. Amer. Chem. Soc.*, 1916, **38**, 310—317).—The solubility of the above-named sulphates in ammonium acetate has been determined at 25° for several concentrations of ammonium acetate. A measured volume of the saturated solution was treated with a little sulphuric acid and evaporated to dryness, gently ignited, and weighed. The results show that the more concentrated the ammonium acetate solution the better will be the separation of lead sulphate from the other sulphates. It is to be noted, however, that the solubilities, even of barium and strontium sulphates, are considerable in ammonium acetate as compared with those in water. A criticism of the various methods of separation of the four metals is given, and a new method suggested. This consists in evaporating the solution to 20 c.c., adding 3 c.c. of 2*N*-sulphuric acid and an equal volume of ethyl alcohol. The mixture is left for five minutes and filtered. The precipitate is washed five times with 5 c.c. of boiling 3*N*-ammonium acetate containing 1% of ammonium sulphate. The filtrate is evaporated to a syrupy consistency, 1 c.c. of concentrated sulphuric acid is added, the mixture dried on the water-bath, and ignited. After cooling, 5—10 c.c. of *N*-sodium hydroxide are added, and the mixture rubbed with a rod, filtered, and the filtrate acidified with acetic acid. The addition of potassium chromate to the filtrate gives a yellow precipitate if lead is present. The barium and strontium sulphates are converted into carbonates by boiling with 4*N*-sodium carbonate, and tested in the usual manner. J. F. S.

Detection of Cadmium. Roberto Salvadori (*Ann. Chim. Applicata*, 1916, **5**, 25—26).—Ammoniacal ammonium perchlorate solution (compare A., 1910, ii, 1002) may be used advantageously in place of potassium cyanide for the detection of cadmium. To the nitric acid solution of copper, cadmium, and bismuth sulphides, excess of ammonia solution is added, the bismuth hydroxide being removed by filtration. Addition to the blue filtrate of ammoniacal ammonium perchlorate solution results in the precipitation of cadmiumtetrammine perchlorate, which dissolves in the hot, but is reprecipitated on cooling. When a 20% solution of ammonium perchlorate solution in ammonia solution of D 0·9 is used, 1 part of cadmium salt per 3000 of solution is readily detectable; in cases where less sensitiveness is sufficient, the concentration of the reagent may be lowered to 15%. When the cadmium is mixed with the five-fold proportion of copper, the reaction is delayed, but not prevented. T. H. P.

Rapid Method for the Analysis of Red Lead and Orange Mineral. John A. Schaeffer (*J. Ind. Eng. Chem.*, 1916, **8**, 237—238).—One gram of the sample is stirred with 15 c.c. of nitric acid (D 1·2) until all red colour has disappeared; 10 c.c. of dilute hydrogen peroxide solution (1 part of 3% hydrogen peroxide solution to 3·5 parts of water) are then added and, when the lead dioxide has nearly dissolved, complete solution is effected by the addition of a small quantity of hot water. The solution is now diluted to about 250 c.c. and titrated with standard permanganate solution having an iron value of 0·005. A control titration is made with the same quantities of nitric acid, hydrogen peroxide, and water, and the difference between the two titrations multiplied by 3·058 gives the percentage quantity of red lead in the sample. The difference multiplied by 1·067 gives the percentage of lead dioxide. A convenient chart is given showing the quantities of red lead and lead dioxide corresponding with the volume of permanganate used in the titrations. W. P. S.

Standardisation of the Mercurials. Donald E. Strickland (*J. Ind. Eng. Chem.*, 1916, **8**, 253—257).—The Hempel iodine titration method yields trustworthy results for the estimation of mercury in calomel and mercurous iodide pills and tablets; Rupp's formaldehyde–iodine method may be used for the estimation of mercuric chloride, mercuric iodide, and of mercury in ammoniated mercury ointment. The thiocyanate method is suitable for the analysis of mercurial ointment, mercuric nitrate ointment, and red mercuric oxide ointment. The presence of lactose does not influence the estimation of mercuric iodide by Rupp's method (compare also A., 1911, ii, 824). W. P. S.

Electrolytic Estimation of Mercury in Mercury Oleates. B. L. Murray (*J. Ind. Eng. Chem.*, 1916, **8**, 257).—About 1 gram of the mercury oleate is weighed into a mercury cathode cup, and 20 c.c. of 10% hydrochloric acid and 15 c.c. of toluene are added.

The anode is placed in position and rotated at about 800 revolutions per minute while the mixture is electrolysed for thirty minutes, using a current of 3 amperes and 8 volts. As the electrolysis proceeds, the contents of the cup become heated nearly to the boiling point of some of the constants; it is essential that the heat should be sufficient to melt the mercury oleate, but if the mixture boils too vigorously the cup should be cooled by a bath of cold water. When the mercury is all deposited, the contents of the cup are washed out by siphonation with water, and the metallic mercury is washed with alcohol, dried with ether, and weighed.

W. P. S.

Electrolytic Estimation of Mercury in Mercury Salicylates. B. L. MURRAY (*J. Ind. Eng. Chem.*, 1916, **8**, 258).—About 0·3 gram of the substance is placed in a mercury cathode cup and dissolved in 10 c.c. of sodium sulphide solution (D 1·18). Twenty c.c. of 10% potassium hydroxide solution are then added, and the mixture is electrolysed with a current of 1 ampere and 7 volts, the anode being rotated at 500 revolutions per minute. About thirty minutes are required for the deposition of the mercury. The electrolyte is then decanted, the mercury washed with water, alcohol, and ether, and weighed.

W. P. S.

Volumetric Estimation of Cerium by Means of Potassium Permanganate. VICTOR LENHER and C. C. MELOCHE (*J. Amer. Chem. Soc.*, 1916, **38**, 66—70).—Cerous compounds are oxidised to ceric compounds by potassium permanganate according to the equation: $6Ce(NO_3)_3 + 2KMnO_4 + 4H_2O = 4Ce(NO_3)_4 + 2Ce(OH)_4 + 2KNO_3 + 2MnO_2$. The ceric salt produced hydrolyses readily with the production of free acid, and this tends to make the reaction reversible; hence a base must be added to neutralise this acid. A number of experiments are described, in which various bases are used to neutralise the acid. The titration may be carried out in either hot or cold solution, but it should be generally finished hot and the permanency of the end-point tested by boiling the solution for a minute. Among the substances investigated were zinc oxide, calcium carbonate, magnesium oxide, borax, sodium hydrogen carbonate, sodium carbonate, sodium hydroxide, barium hydroxide, and potassium hydroxide. Of these, zinc oxide and magnesium oxide are by far the most satisfactory. Good results may be obtained with borax and sodium hydrogen carbonate, whilst sodium carbonate yields fair, but not entirely satisfactory, results. The other substances do not give satisfactory results. Sodium acetate, sodium silicate, sodium phosphate, sodium tungstate, and sodium arsenate are entirely unsatisfactory. The method may be used for the estimation of tervalent cerium in the presence of quadrivalent cerium.

J. F. S.

Simple Bath Used for the Solution of Samples in an Oxygen-free Atmosphere. O. L. BARNEBEY (*J. Amer. Chem. Soc.*, 1916, **38**, 374—375).—The bath described was designed for the

solution of minerals in which ferrous iron was to be estimated. It consists of an 8-inch porcelain dish, in which are placed some glass beads and a 5″ circular desiccator plate with supports. On the plate a triangle of heavy glass rod is placed, and this serves to support the dish in which the solution is to take place. The whole is covered with a 6″ funnel which has had its stem cut off. A solution of 1 : 2-phosphoric acid is poured into the dish in such an amount that it just reaches the inside dish. The whole is heated on a sand-bath, and the steam generated expels the air and heats the dish and its contents. The contents of the dish can be stirred by means of a platinum or glass rod through the open end of the funnel. J. F. S.

Analysis of Chromium Oxide. ALLAN J. FIELD (*J. Ind. Eng. Chem.*, 1916, **8**, 238—239).—Fusion with sodium peroxide is recommended, the resulting chromate being then estimated iodometrically. The author finds that the fusion may be carried out in a platinum crucible, without appreciable damage to the latter, if the crucible, containing about 0·5 gram of chromium oxide and 3 grams of sodium peroxide, is placed in a larger porcelain crucible which is heated so that the mixture just melts. The heating should be continued for twenty minutes, the mass then dissolved in water, the solution boiled for twenty minutes, filtered to remove any ferric hydroxide, neutralised with hydrochloric acid, and diluted to 250 c.c. One hundred c.c. of this solution are now treated with 10 c.c. of concentrated hydrochloric acid, 3 grams of potassium iodide are added, and the liberated iodine is titrated with thiosulphate solution. In the absence of sulphates, the chromium may be estimated gravimetrically as barium chromate. The oxide is fused with sodium peroxide as described, the mass dissolved, the solution neutralised with acetic acid, 0·5 c.c. of glacial acetic acid is added, the solution diluted to 400 c.c., and treated while boiling with dilute barium acetate solution, added drop by drop. The barium chromate is collected, washed with dilute alcohol, dried, and weighed. W. P. S.

Use of Hydrofluoric Acid in the Separation of some Heavy Metals from Tin, Antimony, Tungsten, and Molybdenum by Means of the Electric Current. LEROY W. MCKAY and N. HOWELL FURMAN (*J. Amer. Chem. Soc.*, 1916, **38**, 640—652).—Details are given of methods for the electrolytic estimation of a number of metals in the presence of other metals. The electrolyses are all effected in a mixture of nitric acid and hydrofluoric acid. The analyses which have been carried out include the separation of silver from tin and antimony, mercury from tin and antimony, copper from molybdenum, copper from tungsten and molybdenum, lead from tungsten, lead from molybdenum, lead from tungsten and molybdenum, mercury from tungsten, mercury from molybdenum, mercury from tin, antimony, tungsten, and molybdenum, and silver from tin, antimony, tungsten, and molybdenum. The results in all cases are very good, but in some of the cases the

highest degree of accuracy is only obtained when a correction is applied for the amount of platinum contained in the deposit. This is not a large quantity and rarely exceeds 0·5 mg. J. F. S.

Electrometric Titration of Vanadium. GEORGE LESLIE KELLEY and JAMES BRYANT CONANT (*J. Amer. Chem. Soc.*, 1916, **38**, 341—351).—A method is described by which vanadium may be estimated by titration with a ferrous salt, using the sudden change in *E.M.F.* as indicator of the end of the reaction. A quantity of a vanadate is placed in a beaker, dissolved in 175 c.c. of water, and 25 c.c. of sulphuric acid (D 1·4) are added. A platinum electrode, rotary stirrer, and the connecting tube of a calomel electrode are inserted in the solution. The electrodes are connected with a potentiometer, dry cell, and suspension galvanometer in the usual way. Standard ferrous sulphate is then run in from a burette; the galvanometer needle commences to move off the scale, but is brought back by an adjustable resistance in the circuit. This goes on until about three-fourths of the equivalent amount of ferrous sulphate has been added, then the needle remains at rest until the end-point is reached, when it gives a sudden movement. If in the titration an excess of ferrous sulphate has been added, this can be titrated back by potassium dichromate solution until the needle is just brought back to its position of rest. The best conditions for these titrations are low temperature (10°), high acid concentration, and low concentration of chromic and ferric salts. A comparison of the results obtained by this method is made with the results obtained by four of the standard methods. The results are found to be in close agreement. The oxidation of vanadium to the quinquevalent condition by nitric acid has been found unsatisfactory for quantitative purposes. The oxidation by potassium permanganate has been found entirely unsatisfactory for this method in the absence of chromium. The same remark applies to ammonium persulphate. J. F. S.

Behaviour of Antimony Deposits towards Hypochlorite. W. VAUBEL and A. KNOCKE (*Chem. Zeit.*, 1916, **40**, 209—210).—The ordinary hypochlorite test for distinguishing between antimony and arsenic deposits or mirrors yields trustworthy results only when the hypochlorite solution used is freshly prepared. Old hypochlorite solution always contains some chlorite, and this dissolves antimony deposits, such as are obtained in the Marsh apparatus. The antimony deposits or mirrors vary in composition; grey deposits are not soluble in hypochlorite solution containing chlorite, but the black deposits are quite soluble. Black deposits on a porcelain surface become insoluble after some days' exposure to air. W. P. S.

Electrolytic Estimation of Bismuth in Bismuth β-Naphthol. B. L. MURRAY (*J. Ind. Eng. Chem.*, 1916, **8**, 257—258).—A quantity of 0·3 gram of the sample is ignited in a porcelain crucible until all organic matter has been oxidised. The residue, consisting

of bismuth oxide with a small amount of metallic bismuth, is dissolved by heating with a mixture of 4 c.c. of nitric acid (D 1·4) and 5 c.c. of water, and the solution rinsed with water into a mercury cathode cup, the volume of the solution being made up to 20 c.c. The solution is now electrolysed with a current of 4·5 amperes and 6 volts, the anode being rotated at 1000 revolutions per minute; the time required is about forty-five minutes. When all black masses have disappeared, the anode is stopped and the cathode washed without interrupting the current, then dried with ether and alcohol, and weighed. The increase in weight of the mercury cathode is due to the bismuth which has been deposited on and amalgamated with the mercury. W. P. S.

Colorimetric Estimation of Acetylene. E. R. WEAVER (*J. Amer. Chem. Soc.*, 1916, **38**, 352—361).—A colorimetric method for the estimation of small amounts of acetylene is described. The method consists in conducting the gas under examination through an ammoniacal solution of cuprous chloride containing gelatin, alcohol, and hydroxylamine hydrochloride, and comparing the colour of the red colloidal solution so obtained with a suitable standard, which may be either a solution of a red dye or a piece of ruby glass. The most efficient absorbing solution is made by dissolving 0·25 gram of gelatin in hot water, diluting to 500 c.c., and adding 500 c.c. of 95% alcohol and 1·25 grams of hydroxylamine hydrochloride. To 20 c.c. of this solution 10 c.c. of concentrated ammonia and a small amount of cuprous chloride are added. After the absorption of the acetylene, the solution is diluted to 100 c.c. and compared in a colorimeter with the standard. The standard used by the authors consisted of 0·21 mg. of chromoanilbrown-*R*, 0·04 mg. carmoisine-*B*, 2·5 grams of gum arabic, and 100 c.c. of water. A more convenient, although less accurate, standard is a fixed depth of a solution of azolitmin. If 10 c.c. of a solution of azolitmin containing 1 part of the dye in 2500 parts of water are used as standard, the amount of acetylene in 100 c.c. of the colloidal solution may be calculated from the equation $x=0{\cdot}13y+0{\cdot}03$, where x is the number of milligrams of acetylene, and y is the reciprocal of the number of c.c. of colloidal solution required to match the standard. The method is very sensitive. Amounts of acetylene as small as 0·03 mg. may be detected, and amounts up to 2·0 mg. estimated with an accuracy of 0·05 mg. Hydrogen sulphide and large amounts of oxygen and carbon dioxide interfere with the reaction, but these may be removed by passing the gas through a hot alkaline solution of pyrogallol. J. F. S.

Estimation of Cholesterol in Blood. W. R. BLOOR (*J. Biol. Chem.*, 1916, **24**, 227—231).—Three c.c. of whole blood, plasma, or serum are run in a slow stream of drops into about 75 c.c. of a 3 : 1 mixture of redistilled alcohol and ether in a 100 c.c. flask, which is well agitated during the process. After boiling, the contents of the flask are cooled, brought to the mark with alcohol–ether, mixed, and filtered. Ten c.c. of the alcohol–ether extract are

measured into a small beaker and evaporated just to dryness on a water-bath. Any heating after dryness is reached produces a brown colour, which renders the subsequent estimation difficult or impossible. The cholesterol is now extracted from the dry residue by boiling out three or four times with successive small portions (3—4 c.c.) of chloroform and decanting into a 10 c.c. glass-stoppered graduated cylinder. The combined extracts, after cooling, are made up to 5 c.c., 2 c.c. of acetic anhydride and 0·1 c.c. of concentrated sulphuric acid are added, and the solution, after mixing, placed in the dark for fifteen minutes. The colour is then compared in a Duboscq colorimeter with that of a solution similarly prepared from 5 c.c. of a standard cholesterol solution in chloroform containing 0·5 mg. of cholesterol.

The results obtained are always about 20% higher than those afforded by the Autenrieth-Funk method, but are believed to be the more accurate owing to the better extraction of the cholesterol and the avoidance of the long digestion with strong alkali at a high temperature involved in the older method. H. W. B.

Analysis of Morphine Hydrochloride, Standardised Morphine Hydrochloride Solution, and Morphine Syrup. M. FRANÇOIS and E. LUCE (*J. Pharm. Chim.*, 1916, [vii], **13**, 145—155).—In addition to the usual tests and methods prescribed for the analysis of morphine hydrochloride, the authors recommend that the hydrochloric acid be also estimated by titration with silver nitrate solution, using potassium chromate as indicator; the result of this estimation gives the molecular weight of the base, and, consequently, will indicate whether any base other than morphine is present. In the case of morphine hydrochloride solution, the quantity of the salt present is estimated by evaporating a definite volume of the solution and weighing the residue; here again the estimation of the hydrochloric acid is advantageous. Morphine may be separated from morphine syrup by mixing 50 grams of the sample with 50 grams of water, 20 grams of sodium sulphate, and 0·5 gram of asbestos, and then adding 50 c.c. of $N/10$-iodine solution. After thirty minutes the asbestos and the adhering morphine periodide are collected on a cotton-wool filter, the periodide is then treated with sulphurous acid, the solution obtained is rendered ammoniacal, and extracted with amyl alcohol. The amyl alcohol extract is now shaken with dilute hydrochloric acid, the aqueous solution separated, evaporated, and the residue subjected to the usual tests for the identification of morphine. The quantity of morphine present in the syrup is estimated by treating 10 c.c. of the sample with 1 c.c. of 10% iodic acid solution, adding 1 c.c. of ammonia after the lapse of five minutes, and comparing the coloration produced after a further forty-five minutes with that given by a known amount of morphine under similar conditions. W. P. S.

General and Physical Chemistry

The High Frequency Spectra (L Series) of the Elements Polonium, Radium, Thorium and Uranium. MANNE SIEGBAHN and EINAR FRIMAN (*Physikal. Zeitsch.*, 1916, **17**, 61—62).—The spectra of these elements have been examined in continuation of a previous investigation of the *L*-series lines for the elements between tantalum and bismuth. The spectrum of polonium showed two of the characteristic lines (α_1 and β_1), together with others which are possibly due to impurities. The radium spectrum showed only a single line (α_1), whilst several lines were present in the spectra of thorium and uranium. The α_1, α_2, and β_2 lines agree with the relation pointed out by Moseley, according to which the square root of the frequency is a linear function of the atomic number, but other lines appear to deviate from the requirements of the formula.

H. M. D.

The Arc Spectrum of Cassiopeium, Aldebaranium, Erbium, and the Elements Separated from Thulium. JOSEF MARIA EDER (*Chem. Zentr.*, 1916, i, 242—243; from *Sitzungsber. K. Akad. Wiss. Vienna*, IIa, 124).—The wave-length measurements were obtained by the use of a concave grating and comparison with the iron arc spectrum. The light emitted by cassiopeium in the carbon arc is of a brilliant bluish-green colour. Between λ 7237 and λ 2392 two hundred and sixty lines were measured. In addition to the line spectrum, cassiopeium shows a well-developed and characteristic band spectrum.

The green light emitted by aldebaranium in the arc affords a spectrum which contains many more lines than the spectrum of cassiopeium. Of 630 lines which were measured, it is considered probable that 422 belong to aldebaranium, the remainder being due to the presence of cassiopeium and thulium.

Three preparations of thulium obtained by Auer were also examined. The first ("aldebaranium-thulium I") gave a spectrum containing new lines, which are attributed to a new element, *denebium*. The second ("aldebaranium-thulium II") showed for the most part the same spectrum as the original impure thulium, and *neo-thulium* is suggested as the name for the chief element present. The third preparation gave a spectrum containing a new set of lines which are ascribed to a new element, "*dubhium*."

The investigation of preparations of erbium carefully purified by Auer leads to the conclusion that erbium is probably of complex nature, and its resolution may be expected as a result of further investigation.

H. M. D.

The Absorption Spectra of Complex Metal-ammines. I. Absorption Spectra of Aqueous Solutions of Complex Cobalti-ammines and their Chemical Constitution. YUJI SHIBATA (*J. Coll. Sci. Imp. Univ. Tokyo*, 1915, **37**, (2), 1—28).—Spectrophoto-

metric measurements of the absorption of $N/100$ and $N/1000$ aqueous solutions of some twenty-six cobaltiammines have been made, extending over the visible and ultraviolet regions. The substances examined include hexammines, pentammines, tetrammines, triammines, and diammines, and also sodium cobaltihexanitrite.

All the spectrograms show two or three maxima of absorption in the neighbourhood of the frequencies 2000, 3000, or 4000. The absorption band at 2000 is exhibited by all the cobaltiammines as well as by ordinary cobaltic salts, and it is supposed that this band is due to the cobalt atom. The band at 3000 varies according to the nature of the groups with which the cobalt atom is associated, whilst that at 4000 is only exhibited by complex cobalti-compounds which contain the nitro-group. Compounds of similar constitution have closely similar absorption spectra, and if the non-metallic elements in the groups are identical, the size of the substituent group has but little influence on the absorption. In general, spectrochemical isomerides exhibit differences in their absorption, but this is not always the case. The behaviour of such isomerides depends to some extent on the concentration of the solutions.

H. M. D.

Light Absorption and Fluorescence. IV. Change in Absorption with Concentration. E. C. C. Baly and F. G. Tryhorn (*Phil. Mag.*, 1916, [vi], **31**, 417—430. Compare A., 1915, ii, 77, 605, 714).—The relationship between the frequencies of the infra-red and ultraviolet bands pointed out in previous papers has been confirmed by further observations on aqueous solutions of pyridine and ethyl-alcoholic solutions of salicylaldehyde.

The change in the position of the pyridine absorption band on the addition of water reaches a maximum in $10N$-solution. Since this corresponds almost exactly with the formula of the compound, C_5H_5N,H_2O, the shift of the band is to be attributed to the combination of solute and solvent.

Experiments have also been made with pyridine to determine the change in the absorption coefficient with varying concentration, the solvents used being water, ethyl alcohol, $N/5000$-hydrochloric acid, N-hydrochloric acid, and concentrated sulphuric acid. In all cases the absorption coefficient increases at first with the dilution, and attains a maximum which is unaffected by further dilution. If k represents the absorption coefficient at dilution V and K the maximum value of the coefficient, then the experimental results are expressed by the equation $k/K=1-e^{-\alpha V}$ or $\log K/K-k=\alpha V$, in which α is a constant characteristic of the substance and the solvent used. This relation cannot be reconciled with the operation of the mass law, and it is suggested that the equation may possibly find application to other solution phenomena which apparently do not conform to the requirements of the law of mass action.

H. M. D.

Chemical Constitution and Rotatory Power. III. Influence of the Chemical Function of the Substituent Groups. M. BETTI and G. C. CONESTABILE (*Gazzetta*, 1916, **46**, i, 200—210. Compare A., 1907, ii, 661, 726).—The authors have prepared the following further aldehydic derivatives of *d*-aminobenzyl-β-naphthol ($[\alpha]_D$ +58·90°) of the type $OH\cdot C_{10}H_6\cdot CHPh\cdot N:CHR$, the specific rotations being measured for sodium light filtered through dichromate solution:—with o-*chlorobenzaldehyde*, $C_{24}H_{18}ONCl$, shining, massive scales, m. p. 153°, $[\alpha]_D$ −34·56°, exhibiting marked mutarotation; with m-*chlorobenzaldehyde*, white needles, m. p. 138°, $[\alpha]_D$ +68·88°; with p-*chlorobenzaldehyde*, silky needles, m. p. 158°, $[\alpha]_D$ +75·95°; with 2-*chloro*-5-*nitrobenzaldehyde*,

$C_{24}H_{17}O_3N_2Cl$,

white, silky needles, m. p. 197—198°, $[\alpha]_D$ −98·92°; with 2:5-*dichlorobenzaldehyde*, $C_{24}H_{17}ONCl_2$, m. p. 139°, $[\alpha]_D$ −59·74°; with o-*tolualdehyde*, silky, white needles, m. p. 131°, $[\alpha]_D$ −93·01°; with m-*tolualdehyde*, white crystals, m. p. 131°, $[\alpha]_D$ +143·73°, showing mutarotation; with p-*tolualdehyde*, $C_{25}H_{21}ON$, acicular crystals, m. p. 132—133°, $[\alpha]_D$ +196·07°; with m-*hydroxybenzaldehyde*, $C_{24}H_{19}O_2N$, small, white needles, m. p. 164°, $[\alpha]_D$ +102·71°; with m-*methoxybenzaldehyde*, $C_{25}H_{21}O_2N$, m. p. 110°, $[\alpha]_D$ +139·67°; with p-*homosalicylaldehyde*, $C_{25}H_{21}O_2N$, m. p. 181—182°, $[\alpha]_D$ −18·62°, and with its *methylated* derivative, $C_{26}H_{23}O_2N$, m. p. 148°, $[\alpha]_D$ +220·05°; with *veratraldehyde*, $C_{26}H_{23}O_3N$, white, mammillary masses, m. p. 142°, $[\alpha]_D$ +379·57°; with s-*trimethoxybenzaldehyde*, $C_{27}H_{25}O_4N$, white needles, m. p. 157°, $[\alpha]_D$ +421·9°; with o-*acetylaminobenzaldehyde*, crystalline powder, m. p. 198—200°; with p-*dimethylaminobenzaldehyde*, $C_{26}H_{24}ON_2$, slender, white needles, m. p. 219—220°, $[\alpha]_D$ +704·21°.

These results confirm the conclusions previously drawn concerning the influence on the rotatory power of the chemical functions of the groups united to the asymmetric carbon atom. Gradual increase of the acid character of the aromatic aldehyde residue by introduction of different substituent groups is accompanied by gradual diminution of the molecular rotation, which finally becomes increasingly negative. Thus, the effect of the hydroxyl group is much less than that of a chlorine atom, and the latter is far more effective in the ortho- than in the meta- or para-position. Where, however, the substituent groups diminish the acid character of the aldehyde residue, the rotation undergoes displacement towards the positive side; a similar change is effected by replacement of a hydroxyl group by methoxyl. T. H. P.

Chemical Constitution and Rotatory Power. IV. Substituted Cinnamic Compounds. MARIO BETTI (*Gazzetta*, 1916, **46**, i, 220—225. Compare preceding abstract).—The compound, $OH\cdot C_{10}H_6\cdot CHPh\cdot N:CH\cdot CH:CHPh$, and its derivatives substituted in the benzene nucleus have now been examined. Thus, *d*-aminobenzyl-β-naphthol yields the compounds: with *cinnamaldehyde*, $C_{26}H_{21}ON$, minute, straw-yellow crystals, m. p. 156°, $[\alpha]_D$ +478·04°;

with p-*nitrocinnamaldehyde*, $C_{26}H_{20}O_3N_2$, filbert-coloured needles, m. p. 140°, $[\alpha]_D$ +395·3°; with o-*nitrocinnamaldehyde*, yellow needles, m. p. 152°, $[\alpha]_D$ +350·1°; with *α-chlorocinnamaldehyde*, $C_{26}H_{20}ONCl$, white, microcrystalline powder, m. p. 138·5°, $[\alpha]_D$ +199·55°; with *α-bromocinnamaldehyde*, minute, straw-yellow crystals, m. p. 116°, $[\alpha]_D$ +146·0°; with *α-chloro*-p-*nitrocinnamaldehyde*, slender, cinnamon-coloured needles, m. p. 124°, $[\alpha]_D$ +85·5; with *α-bromo*-p-*nitrocinnamaldehyde*, microscopic, yellow needles, m. p. 102°, $[\alpha]_D$ +73·8°; with *α-chloro*-o-*nitrocinnamaldehyde*, pale yellow, crystalline powder, m. p. 101—104°, $[\alpha]_D$ +61·5°.

The high dextro-rotation of the cinnamaldehyde derivative is probably due to the presence of the ethylenic linking. The introduction of a nitro-group into the aromatic nucleus of the aldehyde results in a diminution in the magnitude of the dextro-rotation, but the extent of this is not so great as with the benzaldehyde compound; the difference between the effects due to a nitro-group in the ortho- and para-positions is also less in the present case. The effects of chlorine and bromine in the α-position are similar to those previously observed. T. H. P.

Magnetic Rotatory Dispersion in Relation to the Electron Theory. I. The Determination of Dispersional Periods. S. S. Richardson (*Phil. Mag.*, 1916, [vi], **31**, 232—256).—In connexion with a theoretical discussion of the phenomenon of magnetic rotatory dispersion, measurements have been made of the dispersion produced by water, benzene, *m*-xylene, carbon disulphide, and α-bromonaphthalene.

Since theory indicates that the effects of two free periods of vibration are more sharply differentiated in magnetic rotatory dispersion than in ordinary dispersion, the results obtained may be applied to the calculation of ultra-violet free periods. The formula deduced on the assumption that each substance is characterised by a single free period of vibration is found to be inconsistent with the experimental data except in the case of carbon disulphide. For each of the other substances examined the existence of more than one free period appears to be necessary to explain the observations. H. M. D.

Magnetic Rotatory Dispersion in Relation to the Electron Theory. II. The Number of Electrons and Additive Relations. S. S. Richardson (*Phil. Mag.*, 1916, [vi], **31**, 454—478).—A theoretical discussion of the optical properties of substances, with special reference to the derivation of the number of electronic resonators from measurements of natural and magnetic rotatory dispersion. The formulæ are applied to a considerable number of organic substances, and from the calculations it appears that in nearly every case the number of resonators in the molecule is equal to or less than the total number of normal valencies of the component atoms.

In the second part of the paper the correlation of additive

properties in connexion with refraction and magnetic rotation is discussed. Although the necessity for expressing the refraction in terms of the isolation frequencies of the resonators has been generally recognised by the adoption of the Lorenz-Lorentz formula, it is noteworthy that, in the case of magnetic rotation, additive relations have been sought for in terms of the directly measured rotation values. It is probable that the more highly constitutive character of the rotation data is due to this difference in procedure. Whether this is the case or not, the author contends that polarisation effects should be eliminated from the rotation data just as much as from the refraction data, and the contribution of the electrons expressed in terms of the free frequencies.

When the polarisation effect is eliminated, the quantity obtained instead of R for comparative purposes is $R \cdot n/(n^2+2)^2$, in which R is the measured molecular rotation and n the refractive index for the monochromatic light used in the measurements.

In connection with the additivity of the optical properties, the author's views lead to the conclusion that the summation is not merely that of effects produced by the individual atoms or by valency linkings, but of effects which are produced partly by the atoms and partly by the linkings. The electrons concerned in the two cases may be for convenience grouped into two classes, but this differentiation is of no importance in so far as the additivity of the effects which they produce is concerned.

Atomic and linking refractivities have been calculated on the above basis, giving the following values: C, 1·245; H, 0·087; O, 1·013; (CC), 0·415; (CH), 1·353; (CO), 0·574; (OH), 1·173; and it is shown that the observed molecular refractivities of a large number of aliphatic compounds are in good agreement with those calculated additively in terms of the above constants.

H. M. D.

Formation and Decomposition of Carbon Dioxide in Ultraviolet Light. ALFRED COEHN and GUSTAV SIEPER (*Zeitsch. physikal. Chem.*, 1916, **91**, 347—381).—The action of ultraviolet light on carbon dioxide has been determined at various pressures. It is shown that an unchangeable stationary condition is set up with the time on exposing carbon dioxide to ultraviolet light. The wave-length of the active light lies below 254 $\mu\mu$. The decomposition increases with increasing pressure more than is demanded by the law of mass action, as is also the case in the photochemical decomposition of aqueous vapour. The decomposition is inversely proportional to the pressure. The photochemical decomposition of carbon dioxide is very sensitive to traces of water vapour, but in the opposite sense to all other photochemical reactions. For example, in the case where a dry gas is decomposed to the extent of 18%, the merest trace of moisture reduces the amount of decomposition to 0·1%. It is shown that neither formic acid nor formaldehyde is formed, and that the water undergoes no change. On the other hand it is shown that on illuminating a mixture of equal volumes of carbon dioxide and hydrogen with ultraviolet light, form-

aldehyde is produced. It is also found that ozone is stable in ultraviolet light at 240°. The authors are unable to reproduce the results of Chapman (T., 1910, **97**, 2463), in which it is shown that the presence of carbon monoxide increases the amount of ozone produced when oxygen is submitted to ultraviolet light. Carbon dioxide is also shown by the authors to have no effect on the amount of ozone produced. J. F. S.

Long-range α-Particles from Thorium. SIR ERNEST RUTHERFORD and A. B. WOOD (*Phil. Mag.*, 1916, [vi], **31**, 379—386).—A small number of bright scintillations from a strong source of the active deposit of thorium (thorium-B+-C) were observed after passage of the α-rays through a thickness of matter corresponding with 11·3 cm. of air at 15° and 760 mm. These are undoubtedly due to α-particles, in very small proportion and of greater velocity than any previously known, and come from thorium active deposit, for they decay with the normal half-period of 10·6 hours. The rays were caused to pass through 4 mm. of air and a thickness of mica amounting together to the equivalent of 9 cm. of air, and from the most intense source used 20 scintillations per minute were counted. The variation of the number on interposing further screens of aluminium, each equivalent to 1·25 cm. of air, was examined. The number is constant up to 9·3 cm. of air and vanishes at 11·3 cm. A change, however, in the rate of disappearance at 10·2 cm. when the number of scintillations was reduced to about two-thirds the original indicates that two homogeneous groups of α-rays of characteristic ranges are probably present, one-third having maximum range 10·2 cm. and two-thirds 11·3 cm. With this may be compared the two known groups from thorium-C, one-third 5·0 cm. and two-thirds 8·6 cm., which suggests that the 10·2 cm. range particles accompany the 5·0 cm. and the 11·3 cm. the 8·6 cm. It has not yet been proved experimentally, however, that the new α-particles come from thorium-C. The ratio of the total number of new α-particles of extreme range to those of 8·6 cm. was found by counting the ordinary α-particles after thirty-two hours had been allowed to elapse, and was found to be 1 : 6700, which is 1 : 10,000 of the total from thorium-C. The Geiger-Nuttall relation suggests that the period of average life of the atoms yielding the long-range α-particles must be 10^{-13} and 10^{-16} second respectively, and the velocity of the particles 2·18 and 2·26 ($\times 10^9$ cm. per second). F. S.

The Scattering of X-Rays and Atomic Structure. C. G. BARKLA and JANETTE G. DUNLOP (*Phil. Mag.*, 1916, [vi], **31**, 222—232).—The original results on the scattering of X-rays by light elements indicated that, with the exception of hydrogen, which scatters approximately twice as much as other elements, the scattering is proportional to the mass of the matter traversed and independent of its atomic character. Now it appears that it is a function of the number of electrons in the scattering atom, which for the elements helium to sulphur inclusive is almost

exactly half the atomic weight, whilst for hydrogen it is equal to the atomic weight, accounting for the anomaly. The unmodified theory applied to the results for heavier elements would indicate that the atoms of nickel, copper, silver, or tin possess a number of electrons from one to three times the atomic weight, but the simple theory cannot be applied to these cases, for the scattering electrons are assumed to act independently of one another. They will do so the more accurately the shorter the time taken by the *X*-ray to cross the atom, and therefore the effect of using *X*-rays of very short wave-length has been studied. For such rays there is only a very slight increase in the mass-scattering coefficient with atomic weight, but as the wave-length of the radiation is increased the increase of scattering becomes more noticeable until, for long wave-lengths (soft *X*-rays), the increase is very considerable. In the limit, for a long enough wave the n electrons in the atom would act rather as a single charge ne than as n charges each of e, and in the former case should give a scattered radiation n times as great as in the latter. The results with heavy elements are in qualitative agreement with this, and there is a rapid change of scattering power with wave-length as the range of wave-length approaches the atomic diameter. In the experiments the scattering by copper, silver, tin, and lead was examined for primary *X*-rays giving a continuous spectrum between narrow limits of wave-length ranging from 0·3 to 1·0 ($\times 10^{-8}$ cm.). F. S.

An Arrangement for Demonstrating Some Laws of Radioactive Change. PAUL LUDEWIG (*Physikal. Zeitsch.*, 1916, **17**, 145—148).—An arrangement similar to Rutherford's hydraulic model is described, consisting of a number of tubes with holes of various apertures in the bottom, placed one above the other, and supplied at the top with water. The rate of outflow being approximately proportional to the quantity of water in the tube, the heights of water in the successive tubes simulate the quantities of the successive products during the course of radioactive change. F. S.

Ionic Mobilities in Hydrogen. II. W. B. HAINES (*Phil. Mag.*, 1916, [vi], **31**, 339—347. Compare A., 1915, ii, 722).—Experiments have been made on the mobilities of the positive ion and the three different negative ions in hydrogen, specially purified, ionised by α-rays, at a range of pressure from 8 cm. to atmospheric. The effect of time on the hydrogen, freshly purified from cold charcoal, left in the apparatus is very marked. At first it is inferred that the negative ions are all free electrons which diminish in number, and heavier ions of definite mobility appear until only the least mobile is present. The mobility multiplied by the pressure for the two heaviest ions is 1206 and 604·7 respectively, and theoretical considerations lead to the view that the three negative ions are built up of one, three, and six molecules of hydrogen per electronic charge respectively, whilst the positive ion has nine molecules.

The more mobile ions are always the first to disappear as the contamination of the hydrogen by impurities increases, and they are much more sensitive to impurities at higher pressure than at lower. The electrons do not appear to attach themselves readily to hydrogen molecules, and the first step in the formation of negative hydrogen ions is the capturing of the electron by a foreign molecule. F. S.

The Ionisation and Dissociation of Hydrogen Molecules and the Formation of H_3. A. J. DEMPSTER (*Phil. Mag.*, 1916, [vi], **31**, 438—443).—A new method for the production of positive rays is described which involves the use of a Wehnelt cathode, and has advantages over Thomson's method in that any desired potential may be employed, and that the pressure may be reduced at will, and may be varied without changing the potential.

The results of experiments made with 800-volt rays at pressures of 0·01, 0·0017, and 0·0005 mm. pressure of hydrogen show remarkable differences when the charge received by the Faraday chamber is plotted as a function of the deflecting magnetic field. The three maxima corresponding with charged particles of the formulæ H, H_2, and H_3 are approximately equally well developed at 0·01 mm. pressure; at 0·0017 mm. the maxima corresponding with H and H_3 are much reduced in comparison with that for H_2, and at 0·0005 mm. the former two have almost completely disappeared.

Since the reduction in pressure is accompanied by a decrease in the number of collisions between positive ions and molecules, the results obtained seem to show that electrons cause ionisation of hydrogen by detaching a single charge from the molecules and are unable to bring about dissociation. The dissociation is due to collisions between positive ions and molecules, and the formation of H_3 is the result of combination between the positively charged atoms and neutral molecules. The quantities of both H and H_3 may therefore be expected to diminish as the pressure of the gas is reduced. H. M. D.

The Periodic System of the Elements. FELIX VON OEFELE (*Pharm. Zentr-h.*, 1916, **57**, 83—84).—The columbium and tantalum of samarskite are regarded as disintegration products of a process in which the helium in the mineral is produced, and the quantity of these three elements leaves open only the probability that they have resulted from the disintegration of compounds of yttrium and cerium with the two higher homologues of manganese. No data are given. F. S.

The Variation of the Radioactivity of the Hot Springs at Tuwa. A. STEICHEN (*Phil. Mag.*, 1916, [vi], **31**, 401—403).—Experiments on a spring at Tuwa, Kaira district, 319 miles north of Bombay, give a result the opposite of those recorded by Ramsey for two Indiana springs (this vol., ii, 5). The springs are both hot and cold; highest temperature 67° and lowest 28°. In April, when the flow was much less than in December, the emanation

content of one of the hot springs was double that in December. The emanation content of the neighbouring wells diminished with their distance from the springs, as though the radium-bearing layer is confined to the springs. The variation would be accounted for if the supply of total emanation to the water is constant throughout the year. F. S.

The Absorption of Gases in Vacuum-Tubes and Allied Phenomena. S. BRODETSKY and B. HODGSON (*Phil. Mag.*, 1916, [vi], **31**, 478—490. Compare A., 1912, ii, 725).—The experiments described are, on the whole, most satisfactorily explained on the assumption that the absorption is due to mechanical occlusion of the gas in the disintegrated part of the cathode.

In a typical experiment the curve expressing the change in the absorption with time shows a gradually increasing rate of absorption. Since the pressure in the discharge tube gradually falls whilst the cathode fall of potential increases, it follows that the rate of absorption increases with the cathode fall. There is no simple relation between the rate of absorption and the temperatures of the electrodes, and the influence of the length of the discharge is such that, for a given current, the absorption is more rapid for a short column than for a long column. This would seem to militate against the theory that absorption is due to chemical action between the gas and the glass walls of the discharge tube.

With a normal cathode fall no absorption took place when experiments were made with copper electrodes in air, oxygen, hydrogen, and carbon dioxide, but with an abnormal cathode fall absorption occurred, and the rate of absorption was found to increase more and more rapidly as the cathode fall of potential was increased. These observations are in agreement with the disintegration-absorption theory, for it has been previously shown that there is no disintegration when the discharge is normal. They are also in accord with Stark's formula connecting the cathode fall with the pressure (compare *Physikal. Zeitsch.*, 1902, **3**, 274).

Although the exact relation between the rate of absorption and the cathode fall is a matter of conjecture, it would seem that the rate of absorption is approximately proportional to the excess energy of the bombarding ions as compared with the energy corresponding with normal discharge. H. M. D.

The Extrapolation of Conductance Values. MERLE RANDALL (*J. Amer. Chem. Soc.*, 1916, **38**, 788—792).—When the percentage ionisation values of salts are plotted against the square root of ion concentrations, the curves obtained fall into non-intersecting groups according to the valence type, and, further, the salts of a single valence type divide themselves into several distinct groups. Thus the haloids of the alkali metals and ammonium form one group, for which α, the degree of ionisation, is nearly the same, and more nearly so as zero concentration is approached. Suppose that for one salt, for example, potassium chloride, the

value a, and also the conductance value Λ, including its value Λ_0 at zero concentration, are accurately known. For another salt of similar type, for example, thallium chloride, a may be assumed to be the same at the same concentration, and if the conductance value Λ be known, Λ_0 can be calculated from the relation $\Lambda_0 TlCl = \Lambda TlCl / aKCl$, since for any salt $\Lambda_0 = \Lambda/a$. Values of Λ_0 can thus be calculated for different concentrations, and the values so obtained, which are nearly constant, can be plotted against square-root concentration. By extrapolating the curve so obtained to zero concentration, a value is obtained for Λ_0 which in the cases examined is practically identical with that obtained by direct methods by different observers. E. H. R.

The Electrical Conductivity of Fused Silver Haloids. RICHARD LORENZ and A. HÖCHBERG (*Zeitsch. anorg. Chem.*, 1916, **94**, 305—316. Compare Lorenz and Kalmus, A., 1907, ii, 430).—The former apparatus has been slightly modified for greater accuracy. Smooth platinum electrodes are used, and the measurements are continued over a range of temperature from 600° to 800°. The conductivity is not quite a linear function of the temperature, and falls with increasing molecular weight.

C. H. D.

Single Potentials in the Silver Cyanide Plating Bath, as Affected by its Composition and Concentration. FRANCIS C. FRARY and RALPH E. PORTER (*Trans. Amer. Electrochem. Soc.*, 1915, **28**, 307—324).—The potentials of various metals and alloys in baths containing varying quantities of silver cyanide and potassium cyanide have been measured against a calomel electrode by a potentiometer method. The conductivity of each solution has also been determined. Chloride or hydroxide has been added in a few cases. The results are tabulated and shown in curves. Iron and brass give uncertain results.

The titration of potassium cyanide solutions with silver nitrate by Liebig's method gives results which are about 3% too low. Hannay's method of titration with mercuric chloride (T., 1878, **33**, 245) is more accurate. C. H. D.

Overvoltage. C. W. BENNETT and J. G. THOMPSON (*J. Physical Chem.*, 1916, **20**, 296—322).—A general discussion of the nature and cause of overvoltage. It is shown that any chemical process which, in generating electricity, takes place in more than one stage, cannot be strictly reversible, but requires more electrical energy to re-form the substances than is given by the reverse reaction. This irreversibility gives rise to excess or overvoltage, since the quantity factor is constant. A general definition of overvoltage is given which has the form:—Overvoltage represents the excess energy required to form a substance over that given by the resolution of the product formed to the original state. It is the amount of energy by which the irreversibility of the process is measured. A new theory of the cause of overvoltage is developed. This

theory is that the excess of the back *E.M.F.* of the system during electrolysis over the reversible *E.M.F.* of the system consisting of the final products is due to the accumulation during such electrolysis of unstable intermediate products above the equilibrium concentration. These products are doubtless active hydrogen H_1, active oxygen O_1 in the case of gases, and active metal M_1 analogous to vaporised metal in the case of metal overvoltages. These products have been shown to be more reactive than the final products, and are sufficiently active to explain the overvoltages found experimentally. Active hydrogen has been shown to be capable of reducing cadmium from cadmium sulphate solutions and zinc from zinc oxide. This theory satisfactorily accounts for the known facts of overvoltage. J. F. S.

A Simple Cell for the Determination of Hydrogen Ion Concentration. J. H. LONG (*J. Amer. Chem. Soc.*, 1916, **38**, 936—939).—A form of cell for the hydrogen electrode is described which can be readily constructed and is quite accurate to 0·5 millivolt, which is sufficient for many purposes. It consists of a glass **Y**-tube, the central arm being much narrower than the other two. Its capacity is 15 c.c., but it contains generally only about 5 c.c. of liquid. The two wide arms are closed by two-holed rubber stoppers coated with paraffin-wax. Liquid is admitted through the central arm, and flows out at one of the wide arms through a capillary tube to the bridge intermediary vessel containing 3·5*N* KCl, which is in turn connected with the calomel electrode. Washed hydrogen is admitted at this wide arm and passes out through a tube inserted in the stopper closing the second wide arm. Through the latter stopper also passes a glass tube filled with mercury, to which the platinised electrode is connected by means of a platinum wire. The cell is fitted up on the hinged arm of a wooden stand, by which means it can be agitated by hand. E. H. R.

The Lead Electrode. FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1916, **38**, 792—801).—In view of the known allotropy of lead, it was important to study the reproducibility of the lead electrode. The combination chosen for examination was Pb–sat. sol. $PbCl_2$-0·1*N* KCl,HgCl–Hg. The lead electrodes were prepared in five different ways: (1) casting the purified lead in sticks; (2) amalgamating cast stick electrodes; (3) depositing lead electrolytically on spirals of platinum wire; (4) depositing lead electrolytically on cast stick electrodes; (5) immersing stick electrodes in an acidified solution of lead acetate. Of these electrodes, the only one reproducible to within 0·3 millivolt was (3), the mean value at 25±0·01° being 0·5219 volt.

Freshly cast sticks of lead, after immersion in an acidified solution of lead nitrate for varying periods of time, lose their ductility and form a grey mass, which is undoubtedly an allotropic modification of lead, but no transition temperature between this and ordinary stick lead could be detected by measurements of *E.M.F.* in 0·2*N* $Pb(NO_3)_2$ as electrolyte at 0° and 25°. Photomicrographs

are given illustrating the transition to the grey form. The normal electrode potential of lead is found to be 0·1318 volt at 25°.

E. H. R.

An Ethylene Electrode. W. F. CLARKE, C. N. MYERS, and S. F. ACREE (*J. Physical Chem.*, 1916, **20**, 286—291).—The *E.M.F.* of an ethylene electrode has been qualitatively studied. The electrode has the form C_2H_4,Pt|0·1*N* HCl|0·1*N* HCl|Pt,Cl_2, and is made up in a U-tube fitted with a tap between the two limbs. Platinum electrodes dip into the acid solution, and the gases are led into the solution at such a depth that they bubble against the surface of the metal plates. A fairly constant value is obtained for the *E.M.F.* in any given cell, but the value varies considerably with different cells. This, according to the authors, is due to the ethylene being impure. When the ethylene is mixed with oxygen the value of the *E.M.F.* drops considerably. The authors consider that the experiments indicate that the combination of chlorine and ethylene is accompanied by an electronic transfer, which can be used to develop an *E.M.F.* The combination is represented by the scheme $CH_2{:}CH_2 + Cl_2 \longrightarrow \overset{+}{C}H_2{\cdot}\overset{+}{C}H_2 + 2\overset{-}{Cl} \longrightarrow CH_2Cl{\cdot}CH_2Cl$: the ethylene losing two electrons to the electrode and then combining with the chlorine ions.

J. F. S.

Oxidation and Reduction. W. F. CLARKE, C. N. MYERS, and S. F. ACREE (*J. Physical Chem.*, 1916, **20**, 292—295).—Qualitative experiments are described on the *E.M.F.* set up in the oxidation of organic substances. The experiments are carried out in a cell similar to that employed in the ethylene electrode (compare preceding abstract). A solution of *N*/5 sodium hydroxide was placed in the U-tube; air was bubbled into one limb and pure oxygen into the other. An oxygen concentration cell of *E.M.F.* 0·0300 volt was thus obtained; on the addition of one drop of formaldehyde to the air side, the *E.M.F.* rose to 0·450 volt; an additional three drops of formaldehyde increased the *E.M.F.* to 0·525 volt. The authors explain the reaction occurring at the electrode in the following manner:

$$\mathrm{H{\cdot}C}\Big\langle\begin{matrix}\mathrm{H}\\\mathrm{O}\end{matrix} + \mathrm{HOH} \longrightarrow \mathrm{H{\cdot}C}\Big\langle\begin{matrix}\mathrm{H}\\\mathrm{OH}\\\mathrm{OH}\end{matrix} : \mathrm{H{\cdot}C}\Big\langle\begin{matrix}\mathrm{H}\\\mathrm{OH}\\\mathrm{OH}\end{matrix} + \mathrm{NaOH} \longrightarrow$$

$$\mathrm{H{\cdot}C}\Big\langle\begin{matrix}\mathrm{H}\\\mathrm{ONa}\\\mathrm{OH}\end{matrix} : \mathrm{H{\cdot}C}\Big\langle\begin{matrix}\mathrm{H}\\\mathrm{ONa}\\\mathrm{OH}\end{matrix} + 2\overset{-}{\mathrm{O}}\mathrm{H} \longrightarrow \mathrm{H{\cdot}C}\Big\langle\begin{matrix}\mathrm{O}\\\mathrm{ONa}\end{matrix} + 2\mathrm{H_2O} + 2\ominus.$$

Experiments are also carried out on the oxidation of phenolphthalin to phenolphthalein. An electrode similarly built up to that described above is used; a little phenolphthalin is dissolved in the alkali in one limb, and the solution electrolysed with an *E.M.F.* of 4·4 volts. A red colour appears at the anode, showing that the phenolphthalin is electrolytically oxidised. The electrode prior to the electrolysis had an *E.M.F.* of 0·176 volt. In another

experiment phenolphthalein was dissolved in the alkali of one limb and hydrogen bubbled in; the red colour became less intense and the cell had an *E.M.F.* of 0·845 volt. J. F. S.

Activity and Concentration: Transport Numbers and Boundary Potentials. ALFRED L. FERGUSSON (*J. Physical Chem.*, 1916, **20**, 326—352).—A long series of *E.M.F.* determinations has been made with solutions of hydrochloric acid. The measurements fall into four groups: (1) the *E.M.F.* between a hydrogen and a calomel electrode in hydrochloric acid of concentration C_1; (2) similar measurements of *E.M.F.*, but in solutions of concentration C_2; (2) the *E.M.F.* between two calomel electrodes, one in hydrochloric acid of concentration C_1 and the other in acid of concentration C_2; (4) similar measurements with hydrogen electrodes. The measurements were made in solutions of concentration $N/5$, $N/10$, $N/60$, $N/90$, $N/120$, $N/180$, and $N/300$ at 18°. From (1) and (2) the free energy of formation of hydrogen chloride from calomel and hydrogen was calculated. From the difference between (1) and (2) the free energy of dilution of hydrogen chloride was calculated. From (3) the *E.M.F.* of the concentration cell having boundary potential with calomel electrodes was obtained, and from (4) the same *E.M.F.* for hydrogen electrodes. The transport numbers were also calculated. From the experiments it is shown that for hydrochloric acid the transport numbers remain constant for dilutions greater than $N/30$, and thus conductivity measurements give an accurate method for determining ion concentrations in dilutions greater than $N/30$, so far as any change in the velocity of the ions is concerned; the concentration is not proportional to the activity; the Nernst equation cannot be applied to an actual concentration cell without some changes, and the formula for calculating boundary *E.M.F.* gives accurate results if the true transport numbers are used and if activity is substituted in place of concentration. J. F. S.

The Migration of Discontinuities in Electrolytic Solutions. M. VON LAUE (*Zeitsch. anorg. Chem.*, 1915, **93**, 329—341).—The theory of Weber and Kohlrausch is stated in a form which is only applicable to completely dissociated solutions. This restriction is now removed, and it is shown that the theory is equally applicable to concentrated, partly dissociated solutions if the assumption be made that the mobility of the ions is independent of the concentration. The ionic concentration in the formula for the transport velocity is then replaced by the total concentration.

C. H. D.

The Structure of Copper Deposits from the Technical Copper Electrotype Process. A. SIEVERTS and W. WIPPLEMANN (*Zeitsch. anorg. Chem.*, 1916, **93**, 287—310).—The deposits previously examined (A., 1915, ii, 216) were obtained in the laboratory. They have now been compared with those obtained from acid baths in the technical processes of preparing electrotypes.

In all cases the deposits are crystalline, the growth of the crystallites being chiefly perpendicular to the surface on which deposition takes place. The structure is finer the higher the current density, but the surface exposed towards the electrolyte is irregular at high current densities, so that the density to be used depends on whether the outer or inner surface of the deposit is required. The coarseness of the outer surface increases with the thickness of the deposit. Rapid deposition gives coarse and often very thick crystals. Copper deposited on a rotating cathode in the Elmore process is finely crystalline and has a laminated structure parallel with the surface of the cathode. Such lamination is observed even where the copper has not been burnished by the rotating agate, and is then attributed to periodic changes in the condition of the bath. The sclerometric hardness, even of the side in contact with the cathode, varies greatly, increasing with the current density and the agitation of the electrolyte. The hardness of the outer surface increases with increasing fineness of structure.

C. H. D.

Paramagnetism and Chemical Dissymmetry. A. QUARTAROLI (*Gazzetta*, 1916, **46**, i, 225—230. Compare A., 1914, ii, 708).—Observations on the compounds of the magnetic elements show that the paramagnetism is greatest for those salts which have the lowest values for the ratio between the saturated valencies and the saturable valencies calculated according to the limiting types of the groups to which the metals belong. This relation becomes still more exact when account is taken of the greater or less facility with which the limited valencies are reached. A number of data are quoted in support of this conclusion. T. H. P.

Calibration of Thermometers. E. WARBURG (*Ber.*, 1916, **49**, 474—476).—The scale of temperature used by the Physikalisch-Technische Reichsanstalt for thermometers and pyrometers is determined (from April 1st, 1916) in the following manner:

(1) In the region between the melting point of mercury and the boiling point of sulphur the temperature is defined by the platinum resistance thermometer; variation of electrical resistance (R) with the temperature (t) is expressed by the equation $R = R_0(1 + at - bt^2)$, the constants being determined by measurement of the resistance at 0°, 100°, and the b. p. of sulphur, which at pressure p is expressed by the formula $444{\cdot}55° + 0{\cdot}0908(p - 760) - 0{\cdot}000047(p - 760)^2$. The following fixed points have been measured on this scale: melting or solidifying points, mercury (−38·89°), tin (+231·84°), cadmium (320·9°), zinc (419·4°); transition temperature of sodium sulphate, +32·38°; boiling points, naphthalene, $217{\cdot}96° + 0{\cdot}058(p - 760)$; benzophenone, $305{\cdot}9° + 0{\cdot}063(p - 760)$.

(2) Below the m. p. of mercury temperatures are defined by means of the platinum resistance thermometer, which Henning has compared with the hydrogen thermometer. The fixed points in this region are determined by the b. p.'s of carbon dioxide

[$-78{\cdot}5° + 0{\cdot}01595(p - 760) - 0{\cdot}000011(p - 760)^2$] and oxygen [$-183{\cdot}0° + 0{\cdot}01258(p - 760) - 0{\cdot}0000079(p - 760)^2$].

(3) Above the b. p. of sulpur the fixed points are determined by the m. p.'s of antimony (630°), silver (960·5°), gold (1063°), copper (1083°), palladium (1557°), and platinum (1764°).

The temperature scale defined in this manner corresponds with the thermodynamic scale, from which, however, it is distinct. The fixed points below 1100° are based on concordant recent measurements with the gas thermometer; the points above 1100° are determined radiometrically and differ somewhat from the values determined by the gas thermometer. H. W.

A Thermoregulator Containing Water. L. HEYDENREICH (*Ann. Inst. Pasteur*, 1916, **30**, 69—75).—A description of a regulator for controlling the heat supplied from a paraffin lamp used to maintain a thermostat at constant temperature. It is used in conjunction with a methylene chloride regulator placed in the thermostat. The regulator and the arrangement of the apparatus are figured in the original paper. W. G.

Entropy in Condensed Substances and its Variations During Changes of State. II. Inorganic Compounds. STEFANO PAGLIANI (*Nuovo Cim.*, 1916, [vi], **11**, i, 118—145. Compare A., 1915, ii, 672, 819).—The author has now extended his considerations to inorganic compounds and since in many cases the specific heats are unknown, especially at low temperatures, the values of the entropy at the melting point have been calculated. In some instances, however, the entropy has been deduced from relations which have been established between the frequencies of binary salts of the alkali metals and those of their components. With such salts it is found, indeed, that the frequency of vibration is proportional to the entropy of unit mass at the melting point, and that the coefficient of proportionality for homologous salts, such as potassium chloride and bromide and sodium chloride, may be regarded as constant and may be calculated by dividing the value for such salts of the numerical coefficient of Lindemann's formula by the ratio of the entropy to the numerical value of the radicle of the same formula; the latter ratio is almost constant and has the mean value 0·44. From the specific frequency of sylvine deduced from Rubens and Hollnagel's optical measurements (A., 1910, ii, 172), Lindemann found the numerical coefficient of his formula to be $4{\cdot}23 \times 10^{12}$ for such salts; this number leads to the value $9{\cdot}6 \times 10^{12}$ for α in the relation $\nu = \alpha S_1$. Further, for binary compounds of the alkali metals, the frequency ν may be calculated from those of the components by means of the expression $\nu/(\nu_1 + \nu_2) = 4/3$.

The results thus obtained show that a periodic relation exists between the values of the entropy at the melting point and the molecular coefficients, the former diminishing as the latter increase. This relation holds more particularly among the terms of a homologous series composed of compounds with either the same positive or the same negative ion. For water at the freezing point the

value of the entropy is relatively low, in accord with the doubled formula. The fact that the very high molecular coefficient of dodecahydrated disodium hydrogen phosphate corresponds with a relatively high value of the entropy is explained by the presence of 63% of water of crystallisation.

For a number of binary compounds the ratio between the entropy of unit mass at the melting point of the compound and the sum of the values for the two components has been calculated. For the salts of the alkali metals this ratio is approximately 1, the values for lithium chloride, sodium bromide, potassium bromide, sodium iodide, and potassium iodide being 0·87, 0·90, 0·84, 0·90, and 0·94 respectively; for other salts, such as silver and thallium chlorides and silver iodide, the value falls to 0·5 or even lower. These differences depend on various factors, especially on the relation between the number of molecules in unit mass of the salt and the sum of the numbers of atoms contained in unit masses of the separate components.

For a large number of salts, including hydrated salts and certain silicates, the change of the entropy during fusion has been calculated, the results showing that in a homologous series ΔS diminishes as the molecular coefficient increases. The low value obtained for nitrogen peroxide indicates that in the solid state the molecule corresponds with the formula $(N_2O_4)_2$, whilst the high value for phosphonium chloride points to dissociation into hydrogen phosphide and hydrogen chloride during fusion; conditions analogous to those of the latter case are encountered in the fusion of hydrated salts, dissociation into lower hydrates taking place. With the silicates, although their molecular coefficients, melting points, and heats of fusion are not exactly determined, there is a tendency to follow the general rule, the variation of the entropy during fusion being greater with the silicates of more simple composition. The excessively low value of ΔS for hydrogen peroxide, namely, 0·010, throws doubt on the value of the heat of fusion employed, namely, 2·7. Further, the heats of fusion for lithium, sodium, and potassium chlorides, deduced from Schemtschuschny and Rambach's cryoscopic measurements (A., 1910, ii, 204), appear to give values of ΔS which are too low in comparison with those for sodium fluoride and sodium and potassium chlorides derived from Plato's results (A., 1906, ii, 521). The value 18·5 found by Goodwin and Kalmus (*Phys. Rev.*, 1909, **28**, 1) for the fusion of lead chloride at 498° also appears too low; the values 45·3 and 25·5 obtained by these authors for sodium and potassium nitrates respectively also give low values for ΔS, and Person's numbers are regarded as more trustworthy. The molecular coefficient for silica lies between those for carbon dioxide and carbon disulphide, and in order that the same may hold for the variation of the entropy during fusion, the value 258·9 and not 135·3 must be taken for the heat of fusion of quartz.

With the compounds investigated by the author the variation of the entropy on fusion diminishes, with equality of molecular coefficient, according to the series: nitrates, fluorides, chlorides,

bromides, hydroxides. In no homologous series could confirmation be obtained of Walden's relation, according to which the quotient of the molecular heat of fusion by the absolute temperature of fusion varies only from 12·5 to 14·8 for compounds regarded as normal (A., 1908, ii, 1014), values varying between 77 and 2 being obtained with sixty-six inorganic compounds (compare Tammann, A., 1910, ii, 1022). According to Tammann, the principal variation of the entropy is determined by the variation of energy in the molecule itself by the transformation of its anisotropic into its isotropic form; the author's results indicate that the ease of this transformation increases with the molecular weight. The variation of the entropy on fusion diminishes with the stability, but the accompanying change of volume does not follow the same order; this result is contrary to what was assumed by Tammann, who held that the alterations in volume are arranged in the order of the melting points. According to Hüttner and Tammann (A., 1905, ii, 229), the heats of fusion of salts should be proportional to $ad/g \cdot dt/dz$, where ad is the duration of crystallisation, g the weight of the salt, and dt/dz the velocity of cooling at the melting point; if this be the case, the ratio between the value of the above expression and the corresponding absolute melting point would be proportional to the change of entropy on fusion. With the haloid salts of the alkali metals the values of this ratio are in the proper order, but neither here nor with the sulphates is there proportionality.

For a number of haloid salts and for water, nitrogen peroxide, sulphuric acid and its monohydrate, and decahydrated sodium sulphate, the values of the molecular depression of the freezing point have been calculated from the values of ΔS determined by direct measurement of the heats of fusion; excepting in the case of mercuric iodide, for which the calculated and observed numbers are 55·5 and 40·5 respectively, the results agree well with those determined directly.

For those inorganic compounds for which the heats of vaporisation are known, the change of the entropy on vaporisation has been calculated. According to Trouton's expression, such change of entropy per gram-mol. should be constant, but only in the two homologous series of halogen hydracids and tetrachlorides is this approximately true, the extreme values found being 16 and 32. Further, neither Weinstein's relation, $m(S_2 - S_1) = \text{const.}$ ("Thermodynamik und Kinetik der Körper," 1901), nor de Forcrand's expression for the molecular variation of the entropy during evaporation (A., 1903, ii, 267, 353, 409, 466), is confirmed.

T. H. P.

The Heat of Fusion and Heat of Formation of Intermetallic Compounds. G. D. Roos (*Zeitsch. anorg. Chem.*, 1916, **94**, 329—357).—A method of determining the latent heat of fusion from the form of the cooling curve has been given by Plato (A., 1906, ii, 521). In a modification of this method, the metal, occupying a volume of 5 c.c., is contained in a glass tube enclosed in a

nickel vessel heated by gas, the space between glass and nickel being filled with magnesia. Curves are constructed from the cooling curves to show the velocity of cooling at regular intervals, and the heat of fusion is then calculated from a comparison between the metal or compound under examination and one of known heat of fusion. An atmosphere of hydrogen is used.

The following values for the heat of fusion of intermetallic compounds are obtained, the results being the mean of those obtained when aluminium, zinc, cadmium, and tin are used as standards. The results are given in Cal. per gram: $MgZn_2$, 65·8; Mg_4Al_3, 82·8; $CuAl_2$, 76·45; Cu_2Cd_3, 26·05; $CaZn_{10}$, 76·95; $CaZn_4$, 83·5; MgCd, 9·62; $PbTl_2$, 7·65; $NaHg_2$, 14·7; $NaCd_5$, 16·9; $NaCd_2$, 22·8; Na_2Pb_5, 10·9; NaPb, 16·9; Na_2Pb, 20·0. The heat of transformation of MgCd is found in the same way to be 2·07. In another series the following values are found: $BiTl_{68}$, 7·31; $BiTl_8$, 8·0; Bi_5Tl_3, 10·9.

Control experiments have been made by the calorimetric method, the substance being enclosed in a sealed silica tube, heated to 700°, and plunged into cold water. The values 61·6 for $MgZn_2$ and 74·7 for $CuAl_2$ are obtained in this way. Calculations of the molecular change of entropy show that most intermetallic compounds undergo more or less dissociation on fusion, the amount varying from 5% to 35%, whilst the compound MgCd undergoes association to the extent of 16%.

Attempts have also been made to determine the heat of formation of the same compounds. The solvent used is bromine water, an excess of bromine being also present. The following approximate values, in Cal. per gram-molecule, are obtained: $MgZn_2$, 25; Mg_4Al_3, 165; $CuAl_2$, 32; $CaZn_{10}$, 199; $CaZn_4$, 55·6; Cu_2Cd_3, 48; MgCd, 18; $NaCd_2$, 31; $NaCd_5$, 60·6. When the heats of fusion and of formation, both expressed in Cal. per gram, are compared, the order is found to be the same for both, only MgCd and $CaZn_4$ being exceptions.

The crystals $PbTl_2$, $BiTl_8$, and $BiTl_{68}$, which occur as maxima on the freezing-point curves, are not chemical compounds, as is shown by their heats of fusion. C. H. D.

The Viscosity and Density of Molten Metals and Alloys. M. Plüss (*Zeitsch. anorg. Chem.*, 1915, **93**, 1—44).—The viscosity is measured by the flow through a capillary tube of hard glass, mounted vertically and heated by a vapour jacket or an electric furnace. As some metals form a mirror on the surface of the glass, the time taken for the level to fall from the first to the second mark may be indicated by the breaking of two electrical contacts. Some of the alloys have a considerable viscosity and oxidise readily, even when hydrogen is passed, so wider capillaries have to be used than are desirable for absolute measurements. For this reason, most of the determinations are relative, and not absolute. The necessary corrections are discussed in detail. The minimum time of flow is for pure metals eighty seconds and for alloys twenty seconds, the capillaries in the latter case being of

such size as to give a time of outflow for mercury of about thirteen seconds.

The viscosity of mercury up to 300° is found to agree closely with the results of Koch. The conclusion of Bingham and Harrison (A., 1909, ii, 382) that the fluidity is a linear function of the temperature is not confirmed. The viscosity-temperature curves for tin and bismuth cut one another at 31·2°.

Three series of eutectiferous alloys have also been investigated, namely, lead–tin, tin–bismuth, and lead–antimony. The density of these alloys is determined by weighing an immersed mass of nickel. In the three cases examined, the viscosity is found to be independent of the density. All the alloys exhibit a marked minimum viscosity at the eutectic composition, although the temperature is well above the eutectic point. In the lead–tin series, the density is not far from a linear function of the composition, but the viscosity curve deviates widely, with a sharp, V-shaped depression at the eutectic point. In the tin–bismuth series, the density curve is quite straight, but the viscosity varies in a peculiar manner, showing two pronounced maxima, corresponding with the compounds $BiSn_2$ and Bi_2Sn respectively, with an intermediate minimum at the eutectic. The lead–antimony series has only been investigated over a small range of composition, and exhibits a deep minimum at the eutectic point.

The relatively low results obtained by Arpi (A., 1914, ii, 540) are attributed to the absence of a necessary correction. C. H. D.

The Viscosity of Certain Alcoholic Solutions. O. F. TOWER (*J. Amer. Chem. Soc.*, 1916, **38**, 833—844).—For the purpose of extending the work on the vapour pressures of certain alcoholic solutions (A., 1915, ii, 11), determinations of the viscosities of solutions of lithium chloride, potassium iodide, benzil, and carbamide in methyl and ethyl alcohols at different concentrations have been made. In addition, the viscosities of the pure alcohols and of these in association with small quantities of water have been determined. For ethyl alcohol, viscosity $\eta^{15°}=0·01317$; for methyl alcohol, $\eta^{15°}=0·006292$.

The viscosimeter used was a modified form of the Bingham apparatus (A., 1912, ii, 1144), the time of flow of the liquid through a capillary tube under constant pressure being measured. Most of the determinations were made at 15°; a few were made at 25°, 40°, and 50° to determine the influence of change of temperature. Curves are given showing the increase of viscosity, η, with increase of concentration, c. The steepness of these curves depends on the association of the solute with the solvent, and is greatest for lithium chloride in both alcohols.

The expression $(p-p_1)/pc$, that is, the relative lowering of the vapour pressure divided by the concentration, is a characteristic constant for solutions, and although the corresponding expression for viscosity, $\eta_1-\eta/\eta c$, is not constant for aqueous solutions, it is found to be tolerably constant for these alcoholic solutions. The author terms this expression the "viscosity constant." It increases

with the solvation of the solvent and is almost independent of temperature changes. Benzil gives an abnormally high value in methyl alcohol, probably on account of its known association with this solvent.

The suggestion of Jones and his associates that the negative viscosity observed with certain solutions is to be attributed to the associated character of the solvent is adversely criticised.

E. H. R.

The Internal Friction of Fused Silver Haloids. RICHARD LORENZ and ALEXANDER HÖCHBERG (*Zeitsch. anorg. Chem.*, 1916, **94**, 317—328).—The method used is that of observing the oscillations of a suspended disk of platinum immersed in the liquid (Fawsitt, T., 1908, **93**, 1299). The liquid is enclosed in a thick-walled porcelain tube in a vertical electric furnace, and all observations are made on a falling temperature in order to avoid the action of the heating current in the solenoid on the oscillations. The viscosity-temperature curves are convex to the temperature axis, and the viscosity increases with increasing molecular weight.

C. H. D.

The Properties of Mixed Liquids. II. Phenol-Water and Triethylamine-Water Mixtures. J. LIVINGSTONE R. MORGAN and GUSTAV EGLOFF (*J. Amer. Chem. Soc.*, 1916, **38**, 844—857. Compare *ibid.*, 1915, **37**, 1462).—The surface tensions of these mixtures at different concentrations and temperatures above and below the critical solution points have been determined by the drop-weight method. From these results and the densities of the mixtures the values of the specific cohesion have also been calculated for the phenol–water mixtures.

The property-composition curves for such systems are characterised by the fact that the constituent of the lower surface tension depresses that of the other to such an extent that the maximum amount soluble in the water layer reduces the surface tension of this to a value differing but slightly from that of the other constituent. The smaller the amount necessary to saturate the water layer, the more sudden this effect will have to be. On the other hand, the effect of the liquid of the larger surface tension on that of the other is exceedingly slight, and varies but slightly with the concentration.

Curves are plotted showing the deviation of the property-composition curves from the values calculated from the law of mixtures, for the properties specific cohesion, surface tension, viscosity, and density. Assuming that the maxima of these curves indicate the formation of definite compounds, both surface tension and cohesion indicate the formation of compounds $Ph{\cdot}OH,55H_2O$ and $NEt_3,50H_2O$, and, using results from the literature, both density and viscosity confirm this value for phenol and water. It seems, therefore, that the water layer of such systems must be considered as transformed completely into a compound, the other layer, a solution of the compound in the second liquid, having its surface

tension little affected. The critical solution point is that point at which the compound is completely miscible in the second liquid.

E. H. R.

Adsorption. I. V. Kubelka (*Chem. Zentr.*, 1916, i, 321—322; from *Collegium*, 1915, 389—408).—According to views recently put forward, the tanning of hides involves the adsorption of the tanning agent by the hide substance. In connexion with this adsorption theory, experiments have been made to determine whether the removal of aliphatic acids from aqueous solution by hide substance is similar to the adsorption of these acids by charcoal, cellulose, and other substances.

Aqueous solutions of formic, acetic, propionic, and butyric acids were shaken at a temperature of 19—21° with a weighed quantity of standardised non-chromed hide powder, and the changes in concentration of the acid solution determined.

The results obtained show that the removal of the acids from aqueous solution takes place very rapidly and that a condition of reversible equilibrium is attained in each case. The relation between the quantity of acid removed by a given weight of hide substance and the concentration of the aqueous solution in equilibrium may be represented by the well-known adsorption formula. For the three higher aliphatic acids the adsorption constant β is proportional to the ionisation constant of the acid.

H. M. D.

The Adsorption of Strong Electrolytes. Yukichi Osaka (*Mem. Coll. Sci. Eng. Kyoto*, 1915, **1**, 257—268).—Experiments have been made to determine the adsorption of salts and water by carefully purified animal charcoal from aqueous solutions of alkali metal salts. Weighed quantities of the salt solutions of determined concentration were shaken up with a measured quantity of charcoal at 25° until equilibrium was attained, and the concentration of the residual solution was determined. The amount of water adsorbed from the various solutions was assumed to be the same as that which is adsorbed by the charcoal in contact with saturated water vapour at 25°. The mean of several experiments showed that the adsorbed water amounted to 85% of the weight of the charcoal.

The results obtained for a series of potassium salts, which were examined at different concentrations, show that the quantity of salt adsorbed by 1 gram of charcoal decreases in the series: iodide, bromide, chloride, sulphate. Potassium salts are adsorbed to a greater extent than the corresponding sodium salts.

Attention is directed to the fact that the order in which the anions are arranged in the above series is approximately the same as that presented by the series in which the anions are arranged according to their influence on the surface tension of water and on the coagulation of colloidal solutions.

H. M. D.

The Dissociation Pressures of Mercurous Chloride. ALEXANDER SMITH and ROBERT PEYTON CALVERT (*J. Amer. Chem. Soc.*, 1916, **38**, 801—807).—Measurements of the vapour pressure of mercurous chloride between 309° and 384° are given. The static isoteniscope previously described was used (A., 1910, ii, 1036, 1037; 1914, ii, 628), the confining liquids used being, in the first series, molten nitrates of sodium and potassium, and in the second the eutectic of potassium chloride and silver chloride, containing three mols. of the former to seven of the latter, and melting at 306°. The pressure 760 mm. is reached at 383·7°, a previous determination by Smith and Menzies (A., 1911, ii, 114) having given 382·5°. The results are satisfactorily represented by an equation of the Kirchoff-Rankin-Dupré type.

The entropies of vaporisation to constant molecular concentration for a number of dissociating substances of the types NH_4I, $N(CH_3)_4I$ are calculated and discussed. E. H. R.

The Diffusion of Solids. C E. VAN ORSTRAND and F. P. DEWEY (*U.S. Geol. Survey Professional Paper*, No. **95***G*, 1915).—The experiments of Roberts-Austen on the diffusion of gold in lead (A., 1896, ii, 590) have been repeated with special precautions. The lead cylinders and gold plates are either turned, cleaned from grease, and clamped together, or the gold is deposited electrolytically on the lead. The specimens are heated in a thermostat, and thin discs are then removed by a revolving knife. The results are in good agreement with theory.

The following values, being the means of a large number of results, are obtained for the coefficient of diffusion of gold in solid lead: at 197°, 0·0076; at 150°, 0·0043; at 100°, 0·0002. The first two values are in good agreement with those obtained by Roberts-Austen, but the last is about ten times his value at the same temperature. The penetration of gold into lead may be detected at a depth of 2·5 cm. after fifty-four days at 197°, but the penetration of lead into gold has not been detected at a greater depth than 0·2 mm. This may be largely due to the lack of sensitiveness of the methods of detecting lead in gold.

A few experiments have been made under increased pressure. The lead cylinders, plated with gold, are enclosed in oil and subjected to pressures up to 10,000 atmospheres. The results are variable, but indicate an increase in the rate of diffusion.

C. H. D.

The Microscopic Structure of Semipermeable Membranes and the Part Played by Surface Forces in Osmosis. FRANK TINKER (*Proc. Roy. Soc.*, 1916, [*A*], **92**, 357—372).—The precipitation semipermeable membranes when examined microscopically show a distinct granular structure. Membranes of Prussian blue and copper ferrocyanide have the finest structure, the diameter of the particles being from 0·1 to 0·4 μ; copper silicate showed particles ranging from 0·2 to 0·5 μ; lead silicate, 0·6 to 0·8 μ; peptone tannate, 0·5 to 1·0 μ; whilst barium sulphate and silver

chloride coagulate into particles 3μ or 4μ in diameter. These particles are not simple, but are themselves aggregates of submicroscopic particles, such as are found to be present in a copper ferrocyanide sol, and when examined by the Zsigmondy-Siedentopf ultramicroscope are found to range in size from 50 to 90 $\mu\mu$. The membranes have not the lattice-work structure of an ordinary gel, and their particles are much more closely knit than those of the gel.

The pores in a copper ferrocyanide membrane range from 8 to 60 $\mu\mu$ in diameter, the average being 15 to 20 $\mu\mu$. The membrane does not therefore act osmotically by exerting a selective mechanical blocking action. There is, however, a close connexion between the osmotic properties of a membrane and the extent to which the membrane capillaries are under the control of surface forces. Osmotic effects are probably the result of selective adsorption phenomena occurring at the surface of the membrane and in the capillaries, the membrane being relatively impermeable to solutes which are negatively adsorbed, but permeable to those which are positively adsorbed. This explains the observation that those membranes having the smallest pores (copper ferrocyanide and Prussian blue) are the most efficient semipermeable membranes.

Photographs are given showing the microscopic structures of different membranes. E. H. R.

The Melting Point of Stressed Crystals. MEINHARD HASSELBLATT (*Zeitsch. anorg. Chem.*, 1915, **93**, 75—83. Compare Tammann, this vol., ii, 229).—The reasoning of Poynting and of Niggli (A., 1915, ii, 242) assumes a cycle which is not actually realisable. Where the liquid phase is free to escape there can be no additional pressure on a crystal, and the only influence on the melting point must be that of stress in the crystal. This influence is small, amounting, according to Riecke (*Ann. Physik*, 1895, [iii], **54**, 731), only to 0·017° when the limit of elasticity is reached.

A cycle is possible, to which the equations of Poynting and Niggli are applicable. A vessel contains the pure substance in a molten condition. A semipermeable cell is immersed in this containing the same liquid in which is dissolved an indifferent substance, which does not crystallise under the conditions of the experiment or traverse the membrane. Crystals of the solvent are contained in the inner cell and are in equilibrium with it. An alteration of the pressure on the liquid now alters the melting point, and the difference between the pressures on the liquid and the solid is maintained by means of the osmotic cell. This condition does not correspond with any process in nature except the freezing of cell-sap. C. H. D.

The Coexistence of Phases Subjected to Different Pressures. RUD. WEGSCHEIDER (*Zeitsch. anorg. Chem.*, 1915, **93**, 95—96).—The formulæ obtained by Niggli (A., 1915, ii, 242) may be deduced in a simple manner from the author's formulæ for the influence of non-uniform pressure on equilibrium (A., 1912, ii, 441).

C. H. D.

The Structure of Crystals. PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1916, **94**, 207—216).—In the light of the work of Bragg (compare T., 1916, **109**, 252) and of Pfeiffer's views on the co-ordination of atoms in a crystal (this vol., ii, 228), "central formulæ" are introduced. Thus the characteristic grouping in the crystal of potassium chloride is [K,6Cl] or [Cl,6K], and in calcium fluoride [Ca,8F] or [F,4Ca], such formulæ expressing the number of atoms of the one element immediately surrounding a central atom of the other. In these cases the atoms are the elementary units of the structure. In pyrites, however, the single sulphur atoms are not elementary units. Two sulphur atoms are always so placed that their centre of gravity is a characteristic point in the space-lattice, and the central formula of the crystal is $[Fe,6S_2]$ or $[S_2,6Fe]$. In a similar manner, the formulæ of calcite may be written $\{Ca(6Ca)2[CO_3]\}$ and $\{[CO_3](6[CO_3])2Ca\}$. The elementary units are thus either simple atoms or radicles. C. H. D.

The Formation of a Cellular Network during Crystallisation. C. DAUZÈRE (*Compt. rend.*, 1916, **162**, 597—599).—The author has discovered a cellular network, apparently identical with that noticed by Cartaud on the surface of certain metals rapidly solidified (compare *Compt. rend.*, 1901, **132**, 1327) and studied by Robin (compare *J. Phys.*, 1914, [v], **4**, 37), in a certain number of transparent, crystallised substances. Particularly clear results have been obtained with alkali nitrates crystallised from the fused salt. This network is apparently produced by the undulatory movement which occurs during crystallisation (compare this vol., ii, 229), each cell being a crystal deprived of its rectilinear edges and plane faces, but having the same physical symmetry as the ordinary crystals of the substance. The cells generally have parallel crystallographic axes, and are formed at the moment of the change of state by the waves of crystallisation. W. G.

[The Influence of Imbibed Substances on the Form of Crystals of Ammonium Chloride]. PAUL GAUBERT (*Chem. Zentr.*, 1916, i, 454—455; from *Bull. Soc. franç. Min.*, 1915, **38**, 149—182. Compare this vol., ii, 229).—Foreign substances taken up from solution during the crystallisation process and which are not present in crystalline form are said to be imbibed. The influence of such imbibed substances on the crystalline form of ammonium chloride has been examined. A quantitative comparison of the influence exerted by different substances is made by determining the smallest quantities which give rise to the formation of cubic crystals of ammonium chloride. The majority of the substances which possess this property are metallic chlorides, ammonium salts, or ammonia derivatives, such as acid amides.

The imbibed substances frequently produce changes in the optical properties, and in most cases in the double refraction increases. H. M. D.

The Accelerating Action of Nuclei on the Reduction Mixture of Gold Chloride and Hydrogen Peroxide. ARNE WESTGREN (*Zeitsch. anorg. Chem.*, 1915, **93**, 151—160).—The observation of Zsigmondy (A., 1906, ii, 679) that the reduction of gold chloride is accelerated by the addition of colloidal gold, and that the degree of dispersion of the resulting colloid depends on that of the gold added, has been further examined and confirmed. The size of the added nuclei is without influence. The dispersion is also independent of the quantity of hydrogen peroxide added and of the concentration, unless this is extremely low.

The size of the particles is determined by means of the velocity of sedimentation. The number of particles in the sol formed by the reduction is proportional to the number of nuclei added, provided that the latter is sufficiently large, otherwise new nuclei are formed spontaneously. The reduced gold is therefore deposited entirely on pre-existing nuclei, provided that there are sufficient of the latter. C. H. D.

Determination of Avogadro's Constant from Measurements of the Brownian Movement of Particles in Gold Hydrosols. ARNE WESTGREN (*Zeitsch. anorg. Chem.*, 1915, **93**, 231—266).—A flat, vertical capillary glass cell is used in which the dilute sol is contained. In the case of highly disperse sols the liquid is previously centrifugated. After a few days the vertical distribution of the particles is determined. The value obtained for Avogadro's constant from the sedimentation equilibrium and the directly determined dimensions of the particles is $60{\cdot}52 \times 10^{22}$, and that from the sedimentation equilibrium and the velocity of fall by Stokes's law is $60{\cdot}42 \times 10^{22}$. These results are quite independent of the volume of the particles when the latter is varied in the ratio 1 : 8. The final value may be taken as $60{\cdot}5 \times 10^{22}$. The probable error is estimated to be $\pm 0{\cdot}3 \times 10^{22}$. C. H. D.

Method of Determining the Frequency of Particles of Different Sizes in Disperse Systems. ARNE WESTGREN (*Zeitsch. anorg. Chem.*, 1916, **94**, 193—206).—A very thin, rectangular cell is made by cementing a cover-glass to a slide by means of fibres of picein. The sol is introduced and time is allowed for the particles to assume a regular distribution. The cell is then turned through 90°, so that the particles settle towards one of the longer sides, and counting is then easily performed. The theory of the method is fully discussed and curves of distribution are given. Gold sols prepared by Zsigmondy's method prove to be very uniformly constituted. C. H. D.

A New Method for the Determination of the Distribution of the Particles in Suspensions. SVEN ODÉN (*Kolloid. Zeitsch.*, 1916, **18**, 33—48).—The method described is based on the determination of the weight of the particles which settle out from the suspension after measured intervals of time. In accordance with Stokes's law, the velocity of sedimentation of spherical particles is

connected with the radius of the particles by the equation $v = Cr^2$, where C is a constant which depends on the difference between the densities of the particles and the surrounding medium, and on the viscosity of this medium. If the suspension is homogeneous, the weight (w) of the particles which have reached the base of the containing vessel after time t is directly proportional to the total weight A of the particles, the velocity with which the particles fall, the time t, and inversely proportional to the height h of the liquid as expressed by the equation $w = kArt/h$. By combination with Stokes's equation this may be written $w = CAr^2t/h$. If the suspension is heterogeneous it may be supposed to be divided into a number of fractions, the average radius of which is r_1, r_2, r_3, etc., and for each of these fractions the above relation will hold. By measuring the increase in w after successive intervals of time, it is possible to deduce the weight of the various fractions which correspond with the several radii r_1, r_2, r_3 . . . From this the numbers of the particles in each fraction may be calculated.

The apparatus employed in the experiments consists of a cylindrical vessel containing the suspension, which is kept at constant temperature. Near the base of this vessel, and occupying almost the entire cross-section, is a circular metal plate which is suspended from one arm of a balance. Suitable weights are placed in the pan attached to the other arm. The upward movement of the plate in the suspension is prevented by a catch arrangement, and when it begins to move downwards, as a result of the settling out of the particles of the suspension, the time is automatically registered, and by means of an electric current which is set up further weights are added to the pan on the opposite arm and a second period of the experiment commences.

Special experiments were made to test the validity of the equation $w = CAr^2t/h$ on which the method of determination depends, and these gave entirely satisfactory results.

Suspensions of various kinds have been examined, and the results obtained are shown in the form of curves which indicate the relative frequencies of occurrence of particles of different sizes.

H. M. D.

Colloid Statistics and the Mechanism of Diffusion. M. von Smoluchowski (*Kolloid. Zeitsch.*, 1916, **18**, 48—54).—In any small element of volume of a gas or solution changes take place in the number of particles, the magnitude of which has been investigated by Svedberg in the case of colloidal solutions of gold. Svedberg's results are examined from the point of view of the theory which the author has developed in respect of this microheterogeneity of the fluid state. Not only is the magnitude of the deviations of the concentration from the average of importance, but equal interest attaches to the rate at which these changes in concentration take place. The magnitude of the deviations is determined by the (osmotic) compressibility, whilst the rate of change of the heterogeneity is conditioned by the Brownian motion of the colloidal particles, and decreases therefore with increase in the

viscosity of the solvent medium. It is shown that Svedberg's experimental data are in agreement with theory both in respect of the magnitude of the changes and the rate at which they occur.

Some light is thrown on the mechanism of diffusion by consideration of these local changes in the concentration of colloidal solutions. At first sight it would seem that the changes referred to above, which are of an irregular but oscillatory type, are not likely to afford any satisfactory explanation of diffusion, which is an irreversible phenomenon. An examination of Svedberg's data shows, however, that the frequency with which a particular concentration in the volume element under observation is followed by other concentrations depends on the extent to which the former deviates from the average. If it deviates little, the probability of an increase is about the same as that of a decrease, but if the deviation is considerable, then the chances are greatly in favour of a diminution of the concentration. The actual sequences are shown to be in good agreement with the requirements of the theory of probability, and no difficulty is therefore met with in connexion with the kinetic-molecular interpretation of diffusion.

H. M. D.

Protective Colloids: Cetraria Islandica as Protective Colloid. II. Colloidal Gold. A. GUTBIER, J. HUBER, and E. HUHN (*Kolloid. Zeitsch.*, 1916, **18**, 57—65. Compare this vol., ii, 231).—The protective action of the colloids extracted from Iceland moss on gold solutions, prepared by the reduction of gold chloride by means of hydrazine hydrate, has been examined in detail. The blue and red solutions of colloidal gold which are obtained by this process are shown to be remarkably stable in presence of the organic colloids. The use of water saturated with chloroform is recommended as solvent in the preparation of these solutions. Not only is the growth of moulds prevented by this means, but the stability of the solutions seems to be increased. Protected and sterilised gold solutions obtained in this way afford no evidence of ageing even after long intervals of time.

On addition of alcohol to the solutions coagulation takes place, and coagulates containing from 4% to 86% of gold have been prepared in this way. The solid colloids, which contain less than about 82% of gold, are completely soluble in water.

In reference to the protective action of colloids and the so-called "gold number" (Zsigmondy, A., 1902, ii, 188), which represents the number of mg. of colloid which is just sufficient to prevent the rapid change of 10 c.c. of a standard red solution of colloidal gold into blue or violet on the addition of 1 c.c. of sodium chloride solution, the authors show that, in general, increase in the gold number is accompanied by a diminution in the viscosity of the (protective) colloid, measured in 0·5% solution at 15°. H. M. D.

Protective Colloids: Cetraria Islandica as Protective Colloid. III. Colloidal Palladium. A. GUTBIER, J. HUBER, and J. KRÄUTER (*Kolloid. Zeitsch.*, 1916, **18**, 65—71).—An investiga-

tion of the protective action of the colloidal extract from Iceland moss on solutions of colloidal palladium which resembles closely that described in the preceding abstract. The very stable solutions, on coagulation by the addition of alcohol, yield reversible solid colloids containing large proportions of palladium. Such colloids containing from 30% to 76% of palladium have been prepared. The limit of complete reversibility for the solid colloids appears to be reached when the palladium content amounts to about 70%. H. M. D.

The Equilibrium of a System of Three Components where Two Liquid Phases Co-exist. SHINKICHI HORIBA (*Mem. Coll. Sci. Eng. Kyoto*, 1915, **1**, 269—275).—A theoretical discussion of the conditions of equilibrium in three-component systems for the special case in which there are two co-existing liquid phases.

H. M. D.

The Equilibrium of Nitrosyl Chloride, $2NO + Cl_2 \rightleftarrows 2NOCl$. A Confirmation of the Additive Law of Internal Atomic Heats. MAX TRAUTZ and CLAUS FRIEDRICH HINCK (*Zeitsch. anorg. Chem.*, 1915, **93**, 177—201).—This equilibrium has been studied experimentally by Trautz (A., 1914, ii, 457), Hinck (*Zeitsch. anorg. Chem.*, 1914, **88**, 285), and Vágó (*Inaug. Diss.*, Budapest, 1911), and certain anomalies have been found. A revision of the data shows that equilibrium is rapidly attained from either side between 450° and 600° abs. provided that the initial concentration lies between the following approximate limits: NOCl, $7—14 \times 10^{-3}$ or NO, $5—32 \times 10^{-3}$; Cl_2, $4{\cdot}5—10 \times 10^{-3}$ mols. per litre. In that case, the dissociation constant is independent of the concentration, and the heat change, calculated from the constants at different temperatures, is not appreciably variable with the temperature, and its value coincides exactly with that calculated thermodynamically.

The higher the pressure of chlorine or the lower that of nitric oxide and the higher the temperature the greater the deviation from the theoretical values, the deviations being in such a direction as to indicate that at least one other substance takes part in the equilibrium.

The experimental dissociation constants are from 50 to 160 times higher than the values calculated from the known values of the specific heats, that of chlorine being known and the value for sulphur dioxide being taken as similar to that of nitrosyl chloride. On the other hand, when the calculation is made on the assumption of the additivity of the internal atomic heats of ideal gases, the constants obtained are about half of the theoretical, whilst the experimental error may amount to ten times. The data afford a full confirmation of this law of additivity. C. H. D.

Equilibria in Systems in which Water, a Phenol, and a Base Constitute the Components. G. J. VAN MEURS (*Zeitsch. physikal. Chem.*, 1916, **91**, 313—346).—The heterogeneous equilibria between

phenol, water, and each of the bases, sodium hydroxide, potassium hydroxide, lithium hydroxide, calcium hydroxide, barium hydroxide, and strontium hydroxide have been investigated at 25°; similar measurements have been made for the systems water, resorcinol, and each of the bases potassium hydroxide and barium hydroxide at 30°. The three components in varying quantities were shaken in a thermostat until the required equilibrium had been set up; the solid and the liquid phases were then analysed. The experimental results are expressed in tabular form and also in curves. The first-named six systems exhibit a binodal curve. All the systems examined show isotherms made up of several curves, and these represent solutions which at the experimental temperature are saturated with the solid phase. The following substances occur as solid phases in one or other of the systems examined: $C_6H_5 \cdot OK,2H_2O$, $C_6H_5 \cdot ONa,3H_2O$, $C_6H_5 \cdot OLi,2H_2O$,

$(C_6H_5O)_2Ca,3H_2O$,

$(C_6H_5O)_2Ba,4H_2O$, $(C_6H_5O)_2Sr,4H_2O$, $C_6H_5 \cdot ONa,2C_6H_5 \cdot OH$, and $C_6H_5 \cdot OK,3C_6H_5 \cdot OH$ at 25°, and $C_6H_4(OK)_2,4H_2O$,

$C_6H_4O_2Ba,2H_2O$ (?),

and $OH \cdot C_6H_4 \cdot OK,2H_2O$ at 30°. No basic compounds are found in any case. All the compounds mentioned above are soluble in water without decomposition. Tables of solubilities of these substances at the indicated temperatures are given. From the curves it is seen that by the addition of a base to an aqueous phenol solution, the phenol is eventually to a very large extent thrown out of the solution as phenoxide. On comparing the composition of the boundary solutions, that is, solutions which are saturated with phenol and base, with one another and with a saturated solution of phenol in water, it is seen that the phenol content is much less in alkali solutions than in water, the values being: water, 93·78%; potassium hydroxide, 0·12%; sodium hydroxide, 0·32%; lithium hydroxide, 2·03%; calcium hydroxide, 12·05%; barium hydroxide, 12·65%; and strontium hydroxide, 22·52%. In the solutions of the alkalis the phenol content increases as the content of alkali decreases, whereas with the alkaline earths both phenol and base increase together. The mono-acid bases expel more phenol from solutions than the di-acid bases. At the same time, the incorrectness of the text-book statement, "that phenol is easily soluble in alkali hydroxides," is demonstrated.

J. F. S.

Chemical Resistance. SHINKICHI HORIBA (*Mem. Coll. Sci. Eng. Kyoto*, 1915, **1**, 277—286).—A theoretical paper in which the author shows that chemical resistance, defined by the equation chemical resistance = affinity/velocity, may be calculated by substitution of a value for the affinity of a chemical reaction which is derived from thermodynamic considerations.

By the introduction of the molecular theory, further consideration is given to the reaction $2H_2 + O_2 = 2H_2O$, and it is shown that the chemical resistance in this case depends on (1) the resistance to the dissociation of the elementary molecules, and (2) the

approach of the hydrogen and oxygen atoms within the range of action of the chemical attractive force. H. M. D.

Chemical Reactions in Anisotropic Liquids. I. THEODOR SVEDBERG (*Kolloid. Zeitsch.*, 1916, **18**, 54—56).—Evidence has been obtained that the velocity of a reaction in an anisotropic liquid solvent changes abruptly when the temperature reaches that at which the anisotropic liquid is transformed into the isotropic form. The observations have reference to the rate of decomposition of picric acid in *p*-azoxyphenetole as solvent at temperatures ranging from 140° to 180°, the progress of the reaction being determined by the change in the electrical conductivity of the solution. The nature of the products formed is unknown, but an electrolyte is formed, since the conductivity increases as the reaction proceeds. At a given temperature the conductivity is a linear function of the time, and the marked increase in the rate of change of the conductivity with the time at the clearing point (165°) is shown plainly in the increased slope of the straight lines which are obtained by plotting conductivity against time at the various temperatures of observation. H. M. D.

The Ignition of Gases by Impulsive Electrical Discharge. W. M. THORNTON (*Proc. Roy. Soc.*, 1916, [*A*], **92**, 381—401).—Considering the ignition of gases by impulsive discharge as a function of sparking distance, it is shown that the shorter the distance the greater the spark, so that the volumes of the least igniting sparks are, in a typical case, the same for all spark lengths. Ignition may occur with intense momentary brush discharge, generally with the true disruptive spark. The products of combustion are found to be ionised and to carry a positive charge, except in the case of the combination of hydrogen and oxygen.

In the experiments described the sparking points were set at a fixed distance apart, and the least voltage necessary to ignite different mixtures of a combustible gas and air was determined. Curves were plotted in which the abscissæ were the percentages of gas in the mixture, and the ordinates were the currents in the primary which, when broken, caused a secondary spark which just ignited the mixture. As the magnitude of the current depends on the kind of coil and switch used, the results are only comparative. The gases examined were in four groups: (1) hydrogen, methane, propane, and pentane; (2) ethylene and acetylene; (3) carbon monoxide and cyanogen; (4) coal-gas and a mixture of hydrogen and methane. The ignition of hydrogen, propane, pentane, and carbon monoxide becomes gradually more difficult as the percentage of oxygen is reduced; methane is ignited by the same spark, whatever the percentage of gas may be; acetylene and cyanogen have the stepped atomic type of ignition; whilst ethylene is more inflammable in rich mixtures. Hydrogen and methane in equal volumes are ignited as methane in type, as hydrogen in magnitude. The limits of inflammability of the paraffins are reached,

the upper when the volume of combustible gas is twice that in the mixture for perfect combustion, the lower when the volume of oxygen is twice that for perfect combustion less one atom to the molecule. The ignition of coal-gas is through methane.

The curves are compared with those obtained with other forms of electrical ignition. Four types are found to occur, covering all from the most rapid to the slowest rate of discharge from the poles. The work gives direct evidence that ignition begins by ionisation of the oxygen of the mixture. E. H. R.

[Catalytic Action of Colloidal Platinum on the Union of Hydrogen and Oxygen.] C. PAAL and ANTON SCHWARZ (*J. pr. Chem.*, 1916, [ii], **93**, 106—118.—Compare A., 1909, ii, 990).—The platinum sol used for these experiments was prepared by the method previously described for palladium sols (A., 1904, ii, 180), using sodium protalbate as a protective colloid. The experiments are of two kinds, in one of which the catalyst and the mixed gases are brought together in a gas-burette over mercury, whilst in the other kind the reaction takes place in a shaking vessel separate from the burette. In all experiments the normal mixture ($2H_2:O_2$) was employed, and the temperature was about 17—21°.

In experiments of the first kind, the reaction velocity gradually fell off, and finally stopped altogether, before complete combination had taken place. This was attributed to the poisoning action of the mercury on the catalyst. In the other class of experiment the velocity was found to diminish as the quantity and concentration of platinum was diminished, the quantity used varying from 0·1 to 0·0001 gram and the concentration from $N/23$ to $N/5860$. The relationship between velocity and concentration was, however, by no means proportional, whether the experiments were conducted at rest or with shaking. Compared with platinum sols prepared by Bredig's method, those prepared by this method, using a protective colloid, appear to produce a greater acceleration in the combination of hydrogen and oxygen. E. H. R.

Catalytic Action of Colloidal Metals of the Platinum Group. XV. Oxidation of Carbon Monoxide in the Presence of Colloidal Platinum, Iridium and Osmium. C. PAAL (*Ber.*, 1916, **49**, 548—560. Compare Hofmann and Schneider, this vol., ii, 45). —The behaviour of hydrosols of platinum, iridium, and osmium, prepared according to Paal's method, towards mixtures of carbon monoxide and oxygen has been studied; in all cases the formation of carbon dioxide was observed, whilst, on the other hand, a negative result was obtained with platinum-black.

Wieland (A., 1912, ii, 347) has shown that carbon monoxide is oxidised to carbon dioxide by palladium-black in the presence of moisture, the reaction occurring in the absence of oxygen, and being attributable to the intermediate formation of formic acid. The author considers that a similar explanation may possibly hold good in the case of platinum, but that with iridium and osmium

the result is more probably due to the direct transference of oxygen adsorbed by the colloid to the carbon monoxide.

[With J. GERUM.]—A mixture of carbon monoxide and oxygen remained unchanged in the presence of platinum-black both in the presence and in the absence of water.

Carbon monoxide is slowly oxidised by oxygen in the presence of colloidal platinum containing sodium protalbate as protective colloid. (The solubility of carbon dioxide in dilute solutions of the latter is shown by special experiments to be practically the same as in water.)

[With FERD. BIEHLER.]—The formation of carbon dioxide proceeds rather more slowly with iridium hydrosol than with platinum hydrosol. Analyses of the residual gas disclose a slight deficiency of oxygen. Similar results are obtained when the mixed gases are shaken with the hydrosol.

[With CHRISTIAN GOES.]—Similar experiments, both with the gas burette and with the shaken vessel, have been made with osmium hydrosol. In each case slow formation of carbon dioxide was observed, and a deficiency of oxygen, probably due to absorption of the latter by osmium, noticed in the residual gas. In the second experiment, which was conducted in such a manner that the oxygen was always present in considerable excess, the oxidation was slower and less complete. The velocity of the reaction therefore seems to be more dependent on the concentration of carbon monoxide than on that of oxygen.

Osmium tetrahydroxide hydrosol shows only very feeble catalytic activity towards mixtures of carbon monoxide and oxygen.

As a consequence of the greater surface, the hydrosols obtained by Paal's method have a catalytic activity greater than those employed by Hofmann (*loc. cit.*). H. W.

Catalysis of Hydrogen Peroxide in a Heterogeneous Medium. I. General Considerations; Experiments with Mercury. GEORGES LEMOINE (*Compt. rend.*, 1916, **162**, 580—587. Compare A., 1912, ii, 747; 1915, ii, 626).—The author has repeated Bredig's experiments on the decomposition of hydrogen peroxide in the presence of mercury (compare A., 1903, ii, 279; 1908, ii, 383), using stronger solutions of hydrogen peroxide (106 vols. and 319 vols.). The reactions were carried out in tubes 16 mm. in diameter, using 6 c.c. of hydrogen peroxide and 3 c.c. of mercury. At 15° the evolution of gas was very slight, but slowly accelerated, and at the end of twelve minutes 43 c.c. of gas had been collected. The rhythmic decomposition (compare Bredig, *loc. cit.*) then commenced, the liquid slowly warming up to 53°. There was a temporary production of an oxide of mercury, which formed a layer on the surface of the mercury, at first red and then black. No formation of yellow oxide was observed. This oxide is a temporary product correlative with the catalysis. Yellow oxide of mercury reacts violently with hydrogen peroxide giving mercury and water with apparently an intermediate production of the suboxide Hg_2O.

Using different volumes of hydrogen peroxide with the same amount of mercury in tubes of the same diameter, the results show that the volume of gas evolved in a given time does not increase indefinitely with the depth of the layer of hydrogen peroxide. Thus the stirring produced by the bubbling of the gas does not ensure a complete renewal of the layer of active liquid in contact with the mercury. W. G.

Catalysis of Hydrogen Peroxide in Heterogeneous Medium. II. Experiments with Platinum. GEORGES LEMOINE (*Compt. rend.*, 1916, **162**, 657—663).—A study of the decomposition of hydrogen peroxide in the presence of platinum-black and platinum moss respectively. In the presence of finely divided platinum the decomposition of hydrogen peroxide is regular, the velocity increasing with the weight of the catalyst and with the state of division of each type of catalyst. By extrapolation, comparing platinum-black and platinum moss at the same state of division, the former is found to have a special catalytic action, much more energetic than that of the latter. When the volume of hydrogen peroxide in the presence of a given weight of catalyst is increased there is an increase in the volume of gas evolved, but this increase does not go on indefinitely, the catalysis not being effective at an indefinite height above the surface of the metal. W. G.

Catalytic Hydrogenation of Organic Compounds with Base Metals at Room Temperature. C. KELBER (*Ber.*, 1916, **49**, 55—63).—If a reduced metal, such as nickel, is suitably prepared it can be applied satisfactorily to hydrogenation processes at the ordinary temperature. Thus, although the catalytic activity of nickel obtained by reduction with hydrogen at about 450° is slight, if the carbonate or other nickel compound is previously spread over a suitable supporting material, the product possesses marked activity superior to that of metals prepared at low temperatures in the absence of a supporting substance. Infusorial earth, various finely divided natural hydrated silicates of magnesium and aluminium, and various forms of charcoal prove useful as supporting substances. The hydrogenation can be effected in aqueous or aqueous-alcoholic solutions. The absorption of hydrogen proceeds more slowly in solutions in alcohol, acetone, ether, or ethyl acetate, but the addition of a little water generally produces a marked increase in the velocity of the hydrogenation. Acetic acid also is a satisfactory solvent, but in chloroform solution the combination with hydrogen occurs very slowly (compare Schwarz, Inaug. Diss., Erlangen, 1912).

Curves are given illustrating the relative activity of nickel reduced under various conditions and of colloidal palladium prepared by the method of Kelber and Schwarz (A., 1912, i, 617). Nickel reduced at 450° on a supporting substance is actually more active than the colloidal palladium towards the combination of hydrogen and oxygen during the earlier stages of the process. Nickel prepared by reduction at 310°, although more active than

metal obtained in a similar manner at 450°, is much less active than nickel produced by reduction at 450° on a supporting substance.

In the hydrogenation of sodium cinnamate in aqueous solution, the advantage possessed by the reduced nickel formed on an inorganic carrier is not so marked, but even then such nickel prepared at 450° has almost the same activity as nickel prepared in the absence of such a carrier at 310°.

Other compounds which were submitted to hydrogenation under the influence of reduced nickel at the ordinary temperature were sodium phenylpropiolate, quinine hydrochloride, diphenyldiacetylene, and the sodium soap derived from cottonseed oil.

Cobalt can be used instead of nickel for the above reactions, but the reduction process then occurs rather more slowly. D. F. T.

The Atom and the Molecule. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1916, **38**, 762—785).—Chemical substances may be conveniently classified under two types, polar and non-polar. The non-polar molecule may be considered as one in which the electrons belonging to the individual atoms are held by such constraints that they do not move far from their normal positions, whilst in the polar molecule one or more electrons may pass from one atom to another, thus dividing, or tending to divide, the molecule into two oppositely charged parts. It is shown that all distinguishing properties of the two types are necessary consequences of this assumption. To facilitate the discussion of the differences between polar and non-polar molecules, the theory of the cubical atom, based on the following postulates, is presented.

(1) In every atom is an essential *kernel* which remains unaltered in all ordinary chemical changes and possesses an excess of positive charges corresponding in number with the ordinal number of the group in the periodic table to which the element belongs.

(2) The atom is composed of a kernel and an *outer atom* or *shell* which, in the case of the neutral atom, contains negative electrons equal in number to the excess of positive charges of the kernel, but the number of electrons in the shell may vary during chemical change between 0 and 8.

(3) The atom tends to hold an even number of electrons in the shell, and especially to hold eight electrons, which are normally arranged symmetrically at the eight corners of a cube.

(4) Two atomic shells are mutually interpenetrable.

(5) Electrons may ordinarily pass from one position in the outer shell to another. Nevertheless, they are held in position by more or less rigid constraints, and these positions and the magnitude of the constraints are determined by the nature of the atom and of such other atoms as are combined with it.

(6) Electric forces between particles which are very close together do not obey the simple law of inverse squares.

Each of these postulates is fully discussed, and the theory is then applied to problems of molecular structure. The electron theory of valency, based upon the original assumption of Helm-

holtz, explains satisfactorily the formation only of compounds of the polar type. If, however, we assume, according to postulate (4), that an electron may simultaneously form part of the shell of two different atoms, the difficulty is overcome and all gradations between a completely polar and a completely non-polar molecule can be appreciated. Two electrons held in common by two atoms correspond with the ordinary single bond, and four electrons so held with the double bond. A triple bond between cubical atoms is impossible, and it has to be assumed that in the case of the carbon atom the eight electrons are attracted in pairs, so that pairs of electrons become located at the corners of a tetrahedron.

The colour of chemical compounds is discussed from the point of view of the theory. Coloured substances are those in which the electrons are less firmly constrained and are free to vibrate with a frequency leading to absorption of visible light. E. H. R.

Some Physical Properties of Elements and Simple Compounds. W. HERZ (*Zeitsch. anorg. Chem.*, 1915, **94**, 1—22).—The variation of properties within the separate groups and subgroups of the periodic system is considered and illustrated by tables. The simpler compounds of several of the groups are also included. General conclusions are not reached. C. H. D.

The Atomic Theory. V. The Doctrine of Corresponding States and the Calculation of the Volume at the Absolute Zero from the Liquid Condition. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1916, **94**, 240—254).—A review of the data gives as the probable ratio of the critical volume to the volume at the absolute zero the value 3·75, the value given by van der Waals's equation being 3, whilst that assumed by D. Berthelot is 4. The ratio of the boiling point to the critical temperature is 0·64, this being a mean value which is very closely approached. The ratio of the critical volume to the volume at the boiling point is 1·41. The ratio of the melting point to the critical temperature is 0·45, and of the melting point to the boiling point 0·64, this value being, however, departed from widely in many instances. The ratio of the volumes at the boiling and melting points respectively is 1·17. It is shown that the use of these formulæ enables the volume at the absolute zero to be calculated when the volume at any one temperature is known, together with the boiling point or the melting point. An "ideal" physicochemical substance is one which obeys strictly the law of corresponding states. C. H. D.

The Atomic Theory. VI. The Calculation of the Space Occupied by Molecules in Close Packing, with Remarks on the Known Methods. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1916, **94**, 255—264. Compare preceding abstract).—The volume of the molecules at the absolute zero is, according to van der Waals's equation, one-twelfth of the critical volume, or one-sixteenth according to D. Berthelot. Consideration of the different

modes of close packing shows that the ratio of the total volume occupied by the molecules at the absolute zero to their true volume lies between the limits 1·35 and 4. C. H. D.

The Atomic Theory. VII. Space-Filling and Mobility of Organic Ions. RICHARD LORENZ and I. POSEN (*Zeitsch. anorg. Chem.*, 1916, **94**, 265—287).—An examination of the mobilities of 122 organic ions shows that the values of the mobilities lie, with few exceptions, between two limits, calculated from the space occupied by molecules (extended to ions) as described in the preceding abstracts. Bi- and multi-valent anions form exceptions to the rule. The mean value corresponds very closely with that derived by Reinganum (A., 1900, ii, 135) from the equation of state. The hydration of an ion by a closed layer of water molecules only one molecule thick would reduce the mobility below that actually observed. Ionic volume has to be taken into account in any comparison between ionic mobility and chemical constitution.
C. H. D.

Gas Pressure Regulator. J. R. POWELL (*J. Ind. Eng. Chem.*, 1916, **8**, 367—368).—The apparatus consists of a bell floating in an oil reservoir; these two parts may be made by cutting off the bottoms of two bottles of different sizes. A glass tube from the top of the bell extends into an inclined test-tube containing a small quantity of mercury, the tube passing through a short rubber stopper in the mouth of the test-tube. The tube ends in a Y-tube, the two short branches of which are just above the surface of the mercury. The gas enters the test-tube through a second tube passing through the stopper, passes into the bell, and is conducted from the latter to the burner in the usual way. As the pressure increases in the bell, this rises slightly, thus moving the tube leading into the test-tube, causing the Y-tube to be immersed in the mercury and cutting off the gas supply. When the pressure decreases the bell falls, the Y-tube is raised, and the gas passes as before. W. P. S.

Inorganic Chemistry.

Water in its Different States. III. Molecular Weight of Water in Solution in Certain Anhydrides and in Solutions in General. GIUSEPPE ODDO (*Gazzetta*, 1916, **46**, i, 172—187. Compare A., 1915, ii, 520, 683).—Solvents in which the molecular weight of water has been determined by different investigators may be divided into the following groups: (1) Ammonia bases: *p*-toluidine, urethane, acetamide, dimethylaniline, and cyanamide, which combine with water, giving hydrates, $NHRR^1R^2\cdot OH$. As

will be shown later, the initial molecule of water is the dimeride or dihydrol, H_4O_2, and in solution in these compounds water will have the simple molecular weight 18 if it is all used to form these hydrates, whereas the molecular weight will be greater and approximate to 36 as the proportion of unaltered dihydrol molecules increases. (2) Oxonium bases: methyl oxalate, methyl succinate, veratrole, ethylene oxide, and to some extent urethane. These tend to form the corresponding oxonium hydroxides, $H{\cdot}ORR^1{\cdot}OH$. (3) The acids: acetic, formic, hydrocyanic, sulphuric, chloroacetic, and phenol. With these water forms, partly or wholly, additive compounds, such as $CR(OH)_3$ and $SO(OH)_4$, or oxonium salts, such as $N{:}C{\cdot}OH_3$ and $Ph{\cdot}O{\cdot}OH_3$. The compounds which tend to originate with these three groups are unstable, and their formation is to be attributed to the preponderating mass action exercised by the solvent; with the exception of a few members, they baffle attempts to isolate them in the free state. (4) Neutral compounds: *s*-dicyanoethane, bromoform, *s*-dibromoethane, and nitrobenzene. These solvents appear to be the least suitable for determining the molecular weight of water, since the first three undergo hydrolysis, and nitrobenzene probably acts as an anhydride and combines with water to form the acid, $O{:}NPh(OH)_2$.

In view of the difficulty of finding a solvent with which such latent reactions can be avoided, the author makes use of those with which water evidently reacts, namely, anhydrides; phosphoryl chloride and nitrogen peroxide are chosen, since in reacting they form a large number of cryoscopically active particles, the commencement of the reaction being consequently marked by pronounced and abnormal depression of the freezing point. In phosphoryl chloride the molecular weight of water has been determined cryoscopically prior to or immediately after the beginning of the reaction between solvent and solute; concordant values close to 36 are obtained. In nitrogen peroxide, with small concentrations of water, numbers almost coincident with 36 are also obtained.

The values of the molecular weight of water determined cryoscopically in other solvents by previous investigators have been recalculated by the method of differences, any abnormality of the initial readings being thus prevented from affecting the later ones of a series. The results thus obtained are: with phenol, 21·2; with *p*-toluidine, 33·4—38·8; with chloroacetic acid, 21·1—29·1; with cyanamide, 26·1—33·0; with acetic acid, 22·3—39·9.

T. H. P.

Water in its Different States. IV. Monomeric Water and the Possibility of Existence of Monomeric Life Different from Actual Dimeric Life. GIUSEPPE ODDO (*Gazzetta*, 1916, **46**, i, 188—200).—From the melting and boiling points of the hydrides of the non-metals of the types MH_4, MH_3, MH_2, and MH, by processes of interpolation and extrapolation, the author has deduced the melting and boiling points of the monomerides of some of these hydrides which ordinarily exist in dimeric forms. In this

way the freezing point of monomeric water is found to be approximately $-130°$ and the boiling point $-100°$. Various points suggested by this result are discussed. T. H. P.

Displacement of Acids by Hydrogen Peroxide. JOACHIM SPERBER (*Chem. Zentr.*, 1916, i, 453—454; from *Schweiz. Apoth. Zeit.*, 1915, **53**, 717—720).—If copper foil is brought into contact with hydrogen peroxide solutions of nitrates or sulphates of the alkali or alkaline earth metals, oxygen is evolved after some time and brown cupric hydroxide separates out. The reactions involved are represented by the equations $Na_2SO_4 + H_2O_2 = Na_2O_2 + H_2SO_4$, $Na_2O_2 + 2H_2O = 2NaOH + H_2O_2$, $Cu + H_2SO_4 + H_2O_2 = CuSO_4 + 2H_2O$, $CuSO_4 + 2NaOH = Na_2SO_4 + Cu(OH)_2$. If a crystal or a saturated solution of copper nitrate is added to hydrogen peroxide, oxygen is evolved and brown cupric hydroxide precipitated. This change does not occur, however, if the hydrogen peroxide is added to the crystalline salt or the saturated solution. With copper sulphate, the hydroxide is precipitated independently of the method of mixing.

The action of hydrogen peroxide on green cupric hydroxide leads to the formation of yellow copper peroxide (CuO_2) or brown cupric hydroxide. H. M. D.

The Absolute Density of Hydrogen Bromide Gas. E. MOLES (*Compt. rend.*, 1916, **162**, 686—688).—Hydrogen bromide was prepared (1) by the action of water on phosphorus tribromide, (2) by the action of bromine on hydrogen sulphide, and carefully purified in each case. The density was determined by weighing glass bulbs of known volume filled with the gas at known pressure and at 0°. The mean of twenty-four determinations gave the value 3·6444 grams as the weight of a normal litre of hydrogen bromide. W. G.

A Crystalline Modification of Sulphur Occurring in Spherolites with Helicoidal Winding. PAUL GAUBERT (*Compt. rend.*, 1916, **162**, 554—556).—Sulphur crystallising by solidification from a molten mass may occur in four different crystalline forms, according to the temperature to which it has been heated, the temperature of crystallisation, and the velocity of cooling (compare Brauns, *Jahrb. Min.*, 1899—1900, **13**, 29; Gaubert, *Bull. Soc. franç. Min.*, 1905, **28**, 157). If the sulphur is heated at above 160° and cooled suddenly, a modification is obtained which, contrary to the γ-form produced at the same time, is very slightly birefractive and is blue by diffused light. The blue colour is due to the fibrosity of the spherolites. Amongst these spherolites are some formed by very slender fibres having a spiral winding. They exhibit numerous varieties, but it is possible to obtain perfect spherolites the crystalline particles of which are wound round the mean index n_m. The fibres rarely show more than three turns in the winding, the distance between the coils varying from one spherolite to another, and generally not exceeding 0·2 mm. W. G.

Hydrazine and its Inorganic Derivatives. III. The Sulphates of Hydrazine, with Special Reference to their Double Salts. FRITZ SOMMER and KURT WEISE (*Zeitsch. anorg. Chem.*, 1916, **94**, 51—91. Compare A., 1914, ii, 266).—Hydrazine usually reacts with acids as a mono-acid base, forming salts which are quite similar in constitution to those of ammonium. Only those salts of hydrazine which contain a single molecule of acid form double salts. On the other hand, complex compounds, in which the hydrazine is attached by subsidiary valencies, always contain the base as a diamine.

Hydrazine sulphate is an exception to the above rule, the insoluble sulphate of the diamine being the more stable. The dihydrazinium sulphate is best prepared by stirring a hot solution of the ordinary sulphate with an excess of barium carbonate, the reaction being $2N_2H_6SO_4 + BaCO_3 = (N_2H_5)_2SO_4 + BaSO_4 + H_2O + CO_2$. The solution becomes alkaline, and is then made faintly acid with sulphuric acid and filtered. The filtrate is evaporated and cooled in ice, when a crystalline powder having the composition $(N_2H_5)_2SO_4,H_2O$ separates, and may be recrystallised from water, when it forms large, transparent, doubly-refracting tables. It is much more soluble in water than ammonium sulphate. The solubility curve consists of two branches, intersecting at the transition point between the monohydrate and anhydrous salt, the temperature of which is found by thermal and dilatometric methods to be 47·3°. The anhydrous salt forms long, colourless prisms, m. p. 118·9° (corr.).

The following double salts of dihydrazinium sulphate are described: $Li_2SO_4,(N_2H_5)_2SO_4$, large, transparent prisms; $MgSO_4,(N_2H_5)_2SO_4,4H_2O$; $CaSO_4,(N_2H_5)_2SO_4$, decomposed by water; hydrazinium alum, $(N_2H_5)Al(SO_4)_2$, crystallising in octahedra and more readily soluble than ammonium alum; and hydrazinium chromium alum, $(N_2H_5)Cr(SO_4)_2$, small, dark violet octahedra. Double sulphates are not formed with sodium, potassium, or ammonium.

Whilst these salts closely resemble those of ammonium, the double salts with nickel, copper, zinc, and other bivalent metals are of a quite different type (Curtius and Schrader, A., 1895, ii, 10). They probably have the constitution $\begin{matrix} NH_2\cdot NH_3 \\ NH_2\cdot NH_3 \end{matrix} > M'' < \begin{matrix} SO_4 \\ SO_4 \end{matrix}$. Attempts to determine the constitution experimentally fail, owing to the very slight solubility of the salts and the readiness with which they are decomposed by contact with platinum, which makes determinations of the conductivity impracticable.

When hydrazine sulphate is added to a solution of nickel sulphate, a reddish-violet precipitate of the trihydrazinate is first obtained, but this dissolves to a blue solution, from which blue crystals of a salt, $NiSO_4,N_2H_4,3H_2O$, separate after a day. This salt is insoluble and is stable in air, but is decomposed by heating with water.

The solubility of monohydrazinium sulphate between 20° and

80° has also been determined. Cryoscopic measurements show that it dissociates in solution into three ions. The effect of acids on the solubility has also been determined. It does not yield double salts with other metallic sulphates under ordinary conditions, being largely hydrolysed into dihydrazinium sulphate and sulphuric acid. It dissolves in concentrated sulphuric acid and deposits colourless crystals of $N_2H_6SO_4,H_2SO_4$. A definite double salt is obtained by adding the solid sulphate to a hot, concentrated solution of ammonium sulphate in large excess. Colourless crystals, stable in air but decomposed by water, are obtained having the composition $N_2H_6SO_4,(NH_4)_2SO_4$. This is the first known double salt of monohydrazinium sulphate. C. H. D.

Mechanism of the Azoimide Synthesis from Hydrazine and Nitrous Acid. FRITZ SOMMER and HEINRICH PINCAS (*Ber.*, 1916, **49**, 259—277).—Judging by the many different interpretations of the reaction between hydrazine and nitrous acid, these substances are capable of giving manifold and apparently unconnected products. Thus, Angeli (1893) gave $N_2H_4 + HNO_2 = N_3H + H_2O$, Dennstädt and Göhlichs (1897) gave $3N_2H_4 + 6HNO_2 = 2N_3H + 2N_2O + O_2 + N_2 + 8H_2O$; de Girard and de Saporta (1904) wrote $N_2H_4 + 2HNO_2 = N_2 + 2NOH + 2H_2O$; Frankes (1905) wrote $N_2H_4 + HNO_2 = NH_3 + N_2O + H_2O$, and Dey and Sen (1912) gave $2N_2H_4 + 3HNO_2 = N_2 + 2N_2O + NH_3 + 4H_2O$. It is now shown that the relationships are by no means so involved if the reaction in neutral solutions is clearly differentiated from that in an acid solution.

The reactions in neutral solutions have already been examined (A., 1913, ii, 952), and were shown to be referable to the decomposition of undissociated molecules of hydrazine mono- and dinitrites, thus, $N_2H_5NO_2 = NH_3 + N_2O + H_2O$ and $N_2H_6(NO_2)_2 = N_2O + H_2O + NH_4NO_2 (= N_2 + 2H_2O)$, reactions which are greatly promoted by the presence of nitrous acid. An addition of a free mineral acid would therefore be expected to operate against these reactions by diminishing the concentration of undissociated hydrazine nitrites. The decomposition of *N*-solutions of hydrazine nitrite in the presence of hydrochloric, nitric, and acetic acids of various concentrations at 0° was therefore investigated. It was found that all the nitrous acid disappeared, but not an equivalent amount of hydrazine (as in neutral solutions), and that less ammonia was produced the higher the H-ion concentration. That is, the above decomposition does indeed fall with increasing H-ion concentration. The new reaction, causing the disappearance of nitrous acid, was recognised by the odour of azoimide, thus, $N_2H_4 + HNO_2 = N_3H + H_2O$.

It is also known that azoimide reacts with nitrous acid according to the scheme $N_3H + HNO_2 = N_2 + N_2O + H_2O$ (Thiele, 1908), and the question therefore arises, Can this reaction compete with the above reaction between hydrazine and nitrous acid, that is, does it play a part in Curtius's synthesis of azoimide? Mixtures of hydrazine monosulphate, sodium azide, and sodium nitrite were

treated with hydrochloric, nitric, and acetic acids in order to find how the nitrous acid was divided between the hydrazine and azoimide. Allowing for the azoimide which is naturally produced from the hydrazine (according to the equation at the end of the last paragraph), it is recognised that Thiele's reaction proceeds with greater velocity than Curtius's, and that increasing the acid concentration promotes Thiele's reaction. This was confirmed by experiments in phosphoric acid, which allows of using higher concentrations (sulphuric acid does not dissolve hydrazine sulphate sufficiently). It is definitely established, therefore, that three simple reactions will explain the decomposition of hydrazine by nitrous acid: (I) $N_2H_4 + HNO_2 = NH_3 + N_2O + H_2O$, which is practically nullified in high H-ion concentrations in favour of (II) $N_2H_4 + HNO_2 = N_3H + 2H_2O$, and the secondary reaction (III) $N_3H + HNO_2 = N_2 + N_2O + H_2O$, which is promoted by increasing the acid concentration.

As an outcome of these considerations, rules may be laid down for the improvement of the yield of azoimide. The H-ion concentration must be high and the hydrazine concentration low in order to avoid reaction I, yet the concentration of acid must not be too high, and it would be advisable to have an excess of hydrazine (leaving some unattacked) to help by its mass against reaction III. An experiment is described in which a yield of 76·3% of azoimide (calculated on the hydrazine affected) was obtained.

The inner mechanism of reactions I and II is also discussed. Reasons are advanced for supposing that nitrosohydrazine is the first product, thus, $NH_2{\cdot}NH_2 + O{:}N{\cdot}OH = NH_2{\cdot}N{:}N{\cdot}OH + H_2O$. This is supposed, on good evidence, to exist in two forms, the nitroxyl form, as written, and as the true nitroso-form, $H{\cdot}N{<}^{NO}_{NH_2}$. In strongly dissociated acids the latter form preponderates, leading by a simple condensation to azoimide, whereas the other form would break down into ammonia and nitrous oxide. In a weak acid, like acetic acid, an equilibrium might exist, leading to both reactions I and II, as the analytical experiments completely demonstrated. This view is therefore strongly in favour of the old ring formulation for azoimide. J. C. W.

Blackening of Yellow Phosphorus. WILLIAM NORMAN RAE (*J. Amer. Chem. Soc.*, 1916, **38**, 887—888).—The slight blackening of some sticks of yellow phosphorus kept under water in stone or glass bottles was traced to the formation of copper phosphide. The water probably contained minute traces of copper salts derived either from the water-taps or from the copper tongs with which the sticks had been handled. E. H. R.

The System Phosphorus from the Point of View of the Theory of Allotropy. A. SMITS and S. C. BOKHORST (*Zeitsch. physikal. Chem.*, 1916, **91**, 249—312. Compare A., 1915, ii, 164). —The vapour-pressure curves of molten white and violet phosphorus have been determined, and from the results it is shown

that although these two curves do not join, owing to the impossibility of making pressure measurements between the temperatures 360° and 550° on account of the very great velocity of transformation, yet they belong to one and the same vapour-pressure curve. From this it follows that liquid white phosphorus may be termed supercooled liquid violet phosphorus. A vapour-pressure formula is deduced which represents the experimental results with sufficient accuracy. The value 16·35 Cal. is found for the value of Q_{LG}, and this quantity is a weak temperature function. Making use of the critical temperature of liquid phosphorus, 695°, as found by Wahl, it is shown that the critical pressure is 82·2 atms. From the critical data the size of the phosphorus molecule is shown to be $P_{4\cdot33}$ at the critical point. The vapour-pressure curve of violet phosphorus is determined and shown to be stable over its whole length. In this connexion it is shown that, when the violet phosphorus has not been completely freed from white phosphorus by extraction with carbon disulphide, the vapour pressure is always too high. Above 450° the last traces of white phosphorus are transformed with measurable velocity into violet phosphorus, and the vapour pressure sinks to the value appropriate for the violet phosphorus. It is shown that extraction with carbon disulphide is insufficient for the preparation of specimens of violet phosphorus of similar vapour pressure. The higher the temperature of formation and the longer the heating is continued the more nearly has the material approached the internal equilibrium and the lower is the vapour pressure. A temperature of 550° is sufficiently high to cause this equilibrium to be reached in a few hours. This points to the fact that violet phosphorus possesses no transition point and that there is no reason for regarding red phosphorus as a metastable modification. This substance never exists in internal equilibrium and is not a homogeneous substance. To the substance, previously known as red phosphorus, the authors have applied the term "red-coloured phosphorus," and characterised it as a mixture of mixed crystals of varying composition. The only stable solid modification of phosphorus is violet phosphorus (the metallic phosphorus of Hittorf), and the colour of this depends on the size of the particles, as is shown by the fact that, using the same method of preparation, red specimens and violet specimens are obtained which have the same vapour pressure and specific gravity. Graphically it has been shown that the triple point of violet phosphorus lies at 589·5° and 43·1 atms. An exact experimental determination gives 589·5° as the temperature of the triple point. The vapour-pressure curve corresponds with the Clapeyron formula, from which it follows that the heat of sublimation is not a function of the temperature. The heat of sublimation, Q_{SG}, has the very high value 25·839 Cal. This value is in complete accord with the theory of allotropy, since the vaporisation of violet phosphorus must be accompanied by a strong chemical reaction. The heat of fusion, Q_{SL}, is 15·618 Cal., which also indicates, as is demanded by the theory, that melting is accompanied by a considerable chemical change. A particular con-

firmation of the theory of allotropy is furnished by the fact that when violet phosphorus is rapidly and partly vaporised in a vacuum at a temperature where the internal equilibrium is only slowly set up, a substance of abnormally low vapour pressure is obtained. This experiment proves that the more volatile component has been expelled at a temperature at which it can only slowly be re-formed. The vapour pressure of this substance increases continuously at constant temperature, and after the addition of 0·1% of iodine and heating at 410° the internal equilibrium is again set up and the vapour pressure becomes normal. The *Tx* diagram is constructed on a binary conception of the pseudo-system, and it is shown that although the pseudo-system is doubtless very complicated, yet the majority of the phenomena can be simply and rationally represented on this basis. J. F. S.

Nomenclature of Compounds of Silicon and Boron. ALFRED STOCK (*Ber.*, 1916, **49**, 108—111).—The suggestion is made that the term "silanes" be accepted generally for the saturated compounds of silicon and hydrogen, the various members being distinguished thus: SiH_4, monosilane; Si_2H_6, disilane; Si_3H_8, trisilane; Si_4H_{10}, tetrasilane, etc. The names of other silicon compounds should be derived from these in the usual rational manner of organic nomenclature; thus, Si_2H_4, Si_2H_2, $SiHCl_3$, $SiH_2(OH)_2$, and $HSiO_2H$ would be termed respectively disilene, disiline, trichlorosilane, silanediol, and silanic acid; Si_3Cl_8 would be described as octachlorotrisilane or perchlorotrisilane, whilst the radicles $\cdot SiH_3$, $\cdot Si_2H_5$, and $\cdot Si_2H_3$ would be respectively designated silyl, disilyl, and disilenyl. The term "silicyl" would be restricted to the grouping $\colon SiO$.

In compounds containing carbon and silicon the analogy with the corresponding carbon compounds can be indicated by the use of the term "silico-"; thus, $SiH_3\cdot CH_2Me$ could be termed monosilicopropane, but the description ethylsilane or silylethane is preferable.

The shortcomings of the present disorganised system of nomenclature for silicon compounds are indicated, and the application of the terminology of organic chemistry to silicon compounds of unknown constitution is deprecated. Indeed, it is suggested that in the case of some of the more complex silicon compounds, such as $OH\cdot Si(O\cdot SiOPh_3)_3$, the formula provides as satisfactory a description as any name can do, and the latter may be dispensed with, at any rate for the present.

Similar suggestions are made for boron compounds; BH_4 (unknown) and B_2H_6 would be described as borane and diborane. The terms boryl, boranol, etc., would follow in the same way; the radical $\cdot BO$ would be termed boroyl. D. F. T.

Silicon Hydrides. I. The Silicon Hydrides Resulting from Magnesium Silicide and Acids. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1916, **49**, 111—157).—After reviewing briefly the earlier literature on the hydrides of silicon, the authors come to

the conclusion that not even the simple tetrahydride, SiH_4 (silane, see Stock, preceding abstract), or disilane, Si_2H_6, have been obtained really pure, and that the statements as to the existence of other hydrides are of little value. By careful investigation of the crude gas obtainable by the action of acids on magnesium silicide, the authors have been able to detect the presence of silane, disilane, trisilane, tetrasilane, and probably also pentasilane and hexasilane, the first four being isolated in a pure condition. Contrary to the statement of Lebeau (A., 1909, ii, 138), disilene, Si_2H_4, is not present in the mixture.

In the preparation of magnesium silicide, the course of the reaction and the quality of the product are largely dependent on the state of division of the silica, and the relative proportions of this substance and magnesium. The best conditions are obtained by taking magnesium and silica in the proportion 2 : 1, the latter substance being obtained by heating the hydrated compound. The hydrated silica should yield 0·3—0·5% residue (chiefly sodium salts) when treated with hydrofluoric acid, because the presence of this amount of impurity prevents the dehydrated silica from being too finely divided; a higher content of impurity is disadvantageous. The reaction is effected with quantities of 100 grams of the mixture in a stout iron crucible of 1000 c.c. capacity; as soon as chemical action has commenced, the white-hot contents are covered with a lid, through which a current of hydrogen is passed until the mass has cooled; the product is a blue, crystalline mass.

For the decomposition of the silicide it is important to bring the solid into direct contact with acid and not first to add water, because the hydrides are so sensitive towards alkali that magnesium oxide will exert a harmful effect on the yield of gas (see also Adwentowski and Drozdowski, A., 1912, ii, 44). Full details are given of the special apparatus in which the magnesium silicide and hydrochloric acid were allowed to react at 50—60° with the exclusion of air, the resulting gases being washed by water and then, after drying with calcium chloride and phosphorus pentoxide, condensed in a tube cooled in liquid air. The hydride, SiH_4, exerts a feeble vapour pressure at this temperature, so that small traces of this gas may be lost, but almost the entire quantity is retained, together with the whole of the other hydrides. By careful fractional evaporation, with special apparatus, of which a full description is given, it was possible to separate the constituents. The purity of the first two members of the series was checked by the volume of hydrogen produced by the action of concentrated sodium hydroxide solution, the chemical changes being expressed $SiH_4 + 2NaOH + H_2O = Na_2SiO_3 + 4H_2$ and $Si_2H_6 + 4NaOH + 2H_2O = 2Na_2SiO_3 + 7H_2$. The composition of the other hydrides was proved by decomposition by slow passage through a quartz tube at 800—900°; the silicon hydrides are less easily decomposed than the corresponding boron compounds, and occasionally a very small quantity of silane produced in the decomposition of the more complex homologues escaped from the heated tube and was

collected in a tube cooled by liquid air; when necessary, a correction was made for this.

Pure silane, SiH_4, melts at $-185°$; the liquid has D^{-185} 0·68 and boils at $-112°/760$ mm. Measurement was made of the vapour pressure at small intervals from $-112°$ to $-160°$; the vapour density at 19° was 16·02, the somewhat higher value obtained by Adwentowski and Drozdowski (*loc. cit.*) being doubtless due to the presence of some disilane. The gas has a rather faint, characteristic odour, recalling stibine; it is very stable at the ordinary temperature; its spontaneous inflammation in the air is uncertain, small bubbles, as a rule, failing to fire; in the presence of appreciable quantities of other hydrides of silicon the gas inflames invariably. Water causes a slow decomposition, $SiH_4 + 2H_2O = SiO_2 + 2H_2$, and alkali hydroxides produce a similar but much more rapid change, the silica in this case being obtained as the alkali silicate.

Pure disilane, Si_2H_6, melts at $-132·5°$ to a liquid, D^{-25} 0·686, b. p. $-15°/760$ mm.; the gas has vapour density 31·7 at 21°; the higher vapour density observed by Moissan and Smiles (A., 1902, ii, 318) must have been due to the presence of silicon hydrides of higher b. p. The vapour pressure was measured at small intervals from $-15·7°$ to $-118°$. Disilane is a colourless gas of rather stronger odour than silane; it can be preserved unaltered at the ordinary temperature, but decomposes rapidly at 300°. The gas inflames invariably in the air, sometimes with violent explosion. Like silane, it is decomposed by water and more rapidly by alkali hydroxide solutions, giving hydrogen and silica or alkali silicate. It is very soluble in benzene and carbon disulphide, but the latter solution is especially inflammable, frequently with explosion, on access of air. With chloroform and carbon tetrachloride vigorous reactions are observed accompanied by flame.

Trisilane, Si_3H_8, when cooled in liquid air forms a crystalline solid, m. p. $-117°$; the liquid has D^0 0·725, b. p. 53°/760 mm. The vapour pressure of the substance was measured at intervals from $-70°$ to $+52·6°$. Under normal conditions trisilane is a mobile, colourless liquid, much less stable than silane and disilane, decomposing slowly at the ordinary temperature. It is decomposed slowly by water and more rapidly by sodium hydroxide solution, yielding hydrogen in the general manner. With carbon tetrachloride an even more violent reaction occurs than is given by disilane.

Tetrasilane, Si_4H_{10}, is a colourless liquid, D^0 0·79, m. p. $-93·5°$, b. p. 80—90°/760 mm., vapour density 61·0. The substance closely resembles trisilane in its general properties. Decomposition occurs fairly rapidly at the ordinary temperature. The vapour pressure of the substance was measured over the range $-30°$ to $+10°$.

The small, relatively sparingly volatile residue from which the above hydrides had evaporated probably consisted of *pentasilane*, C_5H_{12}, and *hexasilane*, C_6H_{14}; the former exerts a vapour pressure

of 1·5 mm. at 0° and the latter approx. 1 mm. at the ordinary temperature. The quantities obtained were insufficient for a careful examination, but these compounds appear to resemble their lower homologues, Si_3H_8 and Si_4H_{10}, in their behaviour when heated and towards air, water, and alkali.

The quantities in which the single hydrides are present in the decomposition product of the magnesium silicide decrease with increasing molecular weight of the compounds. About one-fourth of the silicon present in the magnesium silicide is obtained in the form of silicon hydrides, the remainder being converted into "silico-oxalic acid" (Besson, A., 1912, ii, 255). D. F. T.

Water-glass and Alkali Silicates. W. PUKALL (*Ber.*, 1916, **49**, 397—436).—A series of "water glasses" have been made containing from 1 to 6 molecules of SiO_2 to 1 Na_2O or K_2O by melting together very fine glass sand and the hydrogen carbonates of the metals at about 1050° to 1270°. The effect of cold water and of small amounts of steam on these has been examined, and important results have been obtained which have considerable bearing on many interesting questions relating to silicate rocks.

The glasses $K_2O(SiO_2)_{1-5}$ and Na_2O,SiO_2 absorb water on exposure to the air, the first members being very deliquescent. The effect of cold water on the glasses was determined by suspending the substance in a Pukall filtering cell in water for some days, then estimating the weight and composition of the matter which diffused through the cell, and repeating with fresh water until dialysis was complete. The sodium and potassium glasses are about equally soluble, but the solubility falls with increasing silica content. The most important outcome of this part of the investigation was, however, the proof that water decomposes the higher silicates. The silicates obtained by dialysis contain less silica than the glasses. The proportion of silica in them rises at first, however, only to fall again so low as to be below the proportion 1 SiO_2 to 1 M_2O. That is, the long-continued action of water (some experiments lasted for 200 days) is to leave an insoluble residue almost free from alkali.

A study of the effect of much water on the glasses had as its complement an investigation of the action of small amounts. For this purpose, hydrothermal decomposition was resorted to, the glasses being moistened with water (0·2—0·3 c.c. per gram) and heated in sealed tubes at 180—210° (compare Morey, A., 1914, ii, 202, and Pukall, *Silicat.-Zeitsch.*, 1914, **2**, 8). The masses obtained in this way were powdered and digested with water, when insoluble, crystalline products were obtained. These were analysed. In the potassium series the following well-defined crystalline silicates were identified: $K_2SiO_3,2H_2O$ (doubtful); $K_2Si_2O_5,2H_2O$, a soluble salt obtained by crystallising the glass $K_2O,2SiO_2$; and $K_2H_2Si_4O_{10}$, $K_2H_2Si_6O_{14}$, and $K_2H_2Si_8O_{18}$, the insoluble silicates obtained by the action of superheated steam. The latter are true zeolites, for they are gradually attacked by water, silicates richer in alkali being found in the solution, and acids convert them into almost pure silicic acid. Other potassium silicates containing still more

silicic acid have been obtained, and will be described later. In the sodium series the hydrothermal method gave only one definite compound, the disilicate, $Na_2Si_2O_5,\frac{1}{2}H_2O$, which forms very soluble, well-defined hexagonal plates. All the other products were recognised as mixtures of this with silicic acid.

It appears therefore as though there are two distinct classes of alkali silicates, those obtained by fusion and those derived from the glasses by the action of steam. Of the former, $K_2Si_2O_5$, and from $K_2Si_{10}O_{21}$ upwards, with Na_2SiO_3, $Na_2Si_2O_5$, and $Na_2Si_6O_{13}$ upwards, are crystalline substances, whilst of the latter series, besides the doubtful K_2SiO_3, only compounds with even numbers of silicon atoms have been recognised. The former series is regarded, therefore, as derived from metasilicic acid, thus:

$$\begin{array}{c}KO\cdot\underset{\overset{\|}{O}}{Si}\cdot O\cdot\underset{\overset{\|}{O}}{Si}\cdot O\cdot\underset{\overset{\|}{O}}{Si}\cdot OK = K_2Si_3O_7,\end{array}$$

whilst the latter is based on the condensation of the dibasic disilicic acid molecules which result from orthosilicic acid, thus:

$$(OH)_2Si{<}^{O}_{O}{>}Si{<}^{O}_{O}{>}Si{<}^{O}_{O}{>}Si(OK)_2 = K_2H_2Si_4O_{10}.$$

Many applications of these results to further problems are hinted at. For example, it is suggested that the zeolites and felspars are probably not double silicates, but compounds of the second type of alkali silicates with aluminates or ferrites. These silicates may also act in nature as a kind of cement. It is found, for example, that when the more silicious glasses are pressed into cakes with excess of crude sand or clay and then submitted to the above hydrothermal treatment, hard stones are artificially produced. If these are made with potassium silicate they are stable towards water, whereas the sodium silicate preparations soon decay. The economical production of the readily fusible $K_2H_2Si_4O_{10}$ would be an important matter. On the one hand, its slow decomposition by water would make it a more economical source of potassium for plant growth than the soluble salts now used as manures, and on the other hand it would make a useful glaze for pottery, which is the author's objective.

The experiments are fully described, and the paper opens with a summary of the chemical history of the alkali silicates.

J. C. W.

Determinations of the Density of Fused Silver Haloids. RICHARD LORENZ and A. HÖCHBERG (*Zeitsch. anorg. Chem.*, 1916, **94**, 288—300).—The method used is that described by Lorenz, Frei, and Jabs (A., 1908, ii, 156). The silver haloids are fused and then rendered optically clear by the action of free halogen (Lorenz and Eitel, A., 1915, ii, 260). Between 600° and 800° the relation between volume and temperature is a linear one for the chloride, bromide, and iodide. The coefficients of expansion are of the same order, but diminish slightly with increasing molecular weight.

C. H. D.

The Molecular Condition of Fused Silver Chloride. RICHARD LORENZ, A. LIEBMANN, and A. HÖCHBERG (*Zeitsch. anorg. Chem.*, 1916, **94**, 301—304. Compare A., 1908, ii, 1023).—The rise of molten silver chloride in a capillary tube has been determined over the range from 447° to 582°. The constant of molecular energy calculated from these results is $k = 0.8$ instead of 2·12, the value given by Ramsay and Shields for normal liquids. Silver chloride must therefore be regarded as a very highly associated liquid.

C. H. D.

Singular Properties of Soda Lime. I, II, and III. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1916, **51**, 4—26, 59—82, and 263—278).—The author finds that many reactions which take place with sodium or potassium hydroxide or lime, either not at all or only at high temperatures, occur at the ordinary temperature, and sometimes violently when soda lime is employed. Further, soda lime constitutes the most efficient agent to combat poisonous, irritating, or tear-producing gas, since it readily absorbs chlorine, bromine, halogen hydracids, carbon dioxide, sulphur dioxide, carbonyl chloride, cyanogen, hydrogen cyanide, cyanogen chloride, bromide and iodide, sulphur chloride, thionyl chloride, nitrosyl chloride, nitrogen peroxide, hydrogen arsenide, antimonide, sulphide and selenide, mercaptans, thiocyanic acid, indole, scatole, aldehydes, chlorocarbonic esters, aromatic chloro- and bromo-derivatives with the halogen in the side-chain, ethyl bromoacetate and chloroacetoacetate, chloroacetone, bromoacetophenone, acetic anhydride, etc. The soda lime acts far more energetically when recently prepared and stored in a hermetically sealed vessel. In view of its distinctive behaviour it is probable that it contains a compound such as $Ca(ONa)_2$, $OH\cdot Ca\cdot ONa$, or $OH\cdot Ca\cdot O\cdot Ca\cdot ONa$.

One hundred grams of soda lime in fine granules will absorb 1500—2250 c.c. of carbonyl chloride if the latter is passed slowly through it, but samples prepared from marble exhibit a considerably lower absorptive capacity; when saturated with carbon dioxide, soda lime, even when dry, is incapable of arresting carbonyl chloride. The latter is absorbed well by aniline and other compounds, but soda lime appears to be the only absorbent of practical value.

Hydrogen sulphide is readily absorbed by soda lime, which becomes black, possibly owing to the formation of iron sulphide. This reaction is attended with the development of a very considerable amount of heat, and when the current of gas is mixed with air the soda lime becomes incandescent, whilst replacement of the air by oxygen results in a violent explosion. This incandescence is observed only with freshly prepared soda lime, which should consist of granules 1—3 mm. in diameter. One hundred grams of soda lime absorb as much as 35 litres of hydrogen sulphide.

Soda lime also absorbs hydrogen selenide, which produces rapid and intense irritation of the mucous membrane of the nose and is capable of paralysing the sense of smell for some hours or even

days. No investigation has been made on the action of soda lime on hydrogen telluride, which is, however, only slightly poisonous.

Sulphur dioxide is absorbed by soda lime, rapidly at first and subsequently more slowly, 26 litres being taken up by 100 grams. Nitrogen peroxide is absorbed readily, but nitric oxide only slowly and to a limited extent. The mixture of hydrogen chloride, nitrosyl and nitroxyl chlorides, and chlorine obtained from aqua regia is also rapidly absorbed, and the same is the case at first with cyanogen, of which more than 6 litres are absorbed per 100 grams; the employment of soda lime to retain the cyanogen emitted from blast furnaces is suggested. Cyanogen chloride, bromide, and iodide are likewise absorbed.

Soda lime rapidly absorbs carbon dioxide and serves for the removal of the latter from carbon monoxide, which at the ordinary temperature is absorbed but slightly or not at all. Like all porous substances, soda lime absorbs a little ammonia, but forms no compound and allows it to escape; in presence of soda lime, however, ammonia causes at the ordinary temperature reactions which otherwise occur only at high temperatures. Hydrogen phosphide, prepared by passing hydrogen into a flask containing 45—50% potassium hydroxide solution and a few pieces of phosphorus, is spontaneously inflammable, but loses this property when passed through soda lime; the latter also absorbs phosphorus vapour. Hydrogen arsenide and hydrogen antimonide are absorbed by soda lime. The latter may therefore be used to purify the hydrogen obtained by the action of acid on iron or zinc, but it will not remove hydrogen phosphide, which is detected by the green colour of the flame. Soda lime absorbs many of the impurities of coal-gas and takes away its fœtid odour; similar purification and deodorisation occur with acetylene, which is not absorbed by soda lime. T. H. P.

Mixtures of the Alkaline Earths with Alkali Hydroxides. I. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1916, **51**, 372—377).—The incandescence observed when a mixture of air and hydrogen sulphide is passed over soda lime (preceding abstract) also occurs when the latter is replaced by a mixture of lime or, more especially, baryta with sodium or potassium hydroxide, even when the latter is present in relatively small proportion; potassium hydroxide is more effective than sodium hydroxide. A negative result is obtained when the lime or baryta is replaced by glucinum oxide. T. H. P.

The Ternary System Lime—Alumina—Silica. ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1915, **93**, 271—272).—The investigation of this system by Rankin (A., 1915, ii, 50) does not find any place for the compound observed by the author, $8CaO,2SiO_2,Al_2O_3$ (A., 1912, ii, 159, 450, 761; 1915, ii, 453). The detailed study of the system does not disprove the existence of such a compound, as the mixtures examined by Rankin do not include any in the range of composition in question. That the diagram is incomplete is shown by the presence of one curve, marked 18-C in Rankin's

paper, the position of which is not in accordance with the phase rule. C. H. D.

The Extraction of Glucinum from Gadolinite. C. JAMES and G. A. PERLEY (*J. Amer. Chem. Soc.*, 1916, **38**, 875—877).—The mineral, after crushing and powdering, is first decomposed with strong sulphuric acid. The sulphates are dissolved in water and separated from silica by decantation. The rare earths are then precipitated as oxalates, and the iron and glucinum in the filtrate, after oxidation of the oxalic acid, are separated by fractional precipitation of the hydroxides by means of sodium hydroxide. The two metals are first precipitated together, and then the hydroxides are stirred with sufficient acid to dissolve about two-thirds of the whole. All the glucinum is thus dissolved, with some iron, which can be almost entirely precipitated by means of more sodium hydroxide. The last traces of iron are removed by sodium hydrogen sulphide, and the glucinum is precipitated as basic carbonate. E. H. R.

Glucinum Nitride. FR. FICHTER and EMIL BRUNNER (*Zeitsch. anorg. Chem.*, 1915, **93**, 84—94).—In the preparation of metallic glucinum (Fichter and Jablczynski, A., 1913, ii, 594) it is necessary to dehydrate the fluoride thoroughly, adding the sodium fluoride at the end of the evaporation, and fusing to a clear glass, removing any scum. The metal is finally melted in hydrogen in a tungsten tube vacuum furnace. A magnesia or alundum boat is used as a support, but if the temperature should reach 1900° the glucinum reduces magnesia and the volatile magnesium distils. For experiments at high temperatures glucina may be used. This has m. p. 2450±50°, but is very volatile near its melting point. The metal volatilises readily at 1530° under 5 mm. pressure in hydrogen.

Glucinum absorbs nitrogen from 900° upwards, but only a surface layer is formed, so that it is necessary to powder the product and repeat the process many times, in the course of which much oxide is formed. A better result is obtained by using ammonia. In both cases the product has the formula Gl_3N_2. Glucinum nitride is amorphous, but may be fused if heated rapidly to 2200° in nitrogen under atmospheric pressure, and then solidifies to colourless crystals, which scratch glass. It dissociates at 2400°.

The chemical properties are similar to those of aluminium nitride. The compound is stable in air, and is only slowly decomposed by boiling water. Dilute acids and hot concentrated alkali hydroxides decompose it more readily than aluminium nitride.

The nitride usually contains a little carbon, formed by the reaction $3Gl_2C + 2N_2 = 2Gl_3N_2 + 3C$. Direct experiment shows that glucinum carbide absorbs nitrogen at 1250°, or reacts with ammonia at 950—1000°, liberating carbon. A mixture of glucina and carbon yields the nitride at 1900° in nitrogen. Cyanamide compounds are not formed. C. H. D.

A Revision of the Atomic Weight of Zinc. The Electrolytic Determination of Zinc in Zinc Bromide. GREGORY PAUL BAXTER and MERRITT ROY GROSE (*J. Amer. Chem. Soc.*, 1916, **38**, 868—873).—The procedure adopted in this determination was the same as that used for the analysis of cadmium bromide. The zinc obtained from the purified zinc bromide used for analysis showed a faint trace of cadmium, estimated at 0·001%, when its spark spectrum was examined. The mean of eight determinations gives 65·388 as the atomic weight of zinc. In four of these zinc bromide was electrolysed directly, and in the remaining four it was first converted into sulphate, and there is nothing to choose between the results of the two sets of determinations.

E. H. R.

A Study of the Action of Alkali on Certain Zinc Salts by Means of the Hydrogen Electrode. JOEL H. HILDEBRAND and W. G. BOWERS (*J. Amer. Chem. Soc.*, 1916, **38**, 785—788).—It has been shown in previous publications (A., 1913, ii, 721) how the titration of an amphoteric hydroxide, such as aluminium hydroxide, by an alkali can be followed by means of the hydrogen electrode. In applying the method to zinc hydroxide, a solution of the haloid or sulphate in excess of the corresponding acid was titrated with sodium hydroxide. An examination of the curve obtained by plotting volts as ordinates and c.c. of sodium hydroxide as abscissæ brings out the fact that in the acid solutions of the haloids weak acids of the type $HZnCl_3$ must exist. During solution of the zinc hydroxide in alkali hydroxide part is apparently dissolved as a colloid, whilst the remainder reacts as a monobasic acid, the reaction being $H_2ZnO_2 + OH^- = H_2O + HZnO_2^-$.

E. H. R.

A Revision of the Atomic Weight of Cadmium. The Electrolytic Determination of Cadmium in Cadmium Bromide. GREGORY PAUL BAXTER, MERRITT ROY GROSE, and MINER LOUIS HARTMANN (*J. Amer. Chem. Soc.*, 1916, **38**, 857—867).—Further evidence is presented in support of the analyses of cadmium chloride of Baxter and Hartmann (A., 1915, ii, 98), and the results substantiate the value for the atomic weight of cadmium found by Baxter, Hines, and Frevert (A., 1905, ii, 321; 1906, ii, 541). The method used is that involving the electrolysis of cadmium bromide using a cathode of mercury, and weighing the amalgam formed. This method was also employed by Perdue and Hulett (A., 1911, ii, 397, 433), Laird and Hulett (*Trans. Amer. Electrochem. Soc.*, 1913, **22**, 385), and Quinn and Hulett (A., 1914, ii, 127; 1915, ii, 771), who, however, found a considerably lower value for the atomic weight, viz., 112·3. The experiments here recorded give, as a mean of twelve determinations, the value 112·407. The percentage of cadmium in the bromide is found to be 41·290, whilst Baxter, Hines, and Frevert found the percentage of bromine to be 58·708. The sum of the two is 99·998%.

Four samples of cadmium bromide were prepared for analysis

with great care. Metal prepared from them gave a spark spectrum free from any lines but those usually associated with cadmium. After electrolysis the electrolyte was always evaporated with a little sulphuric acid, and a very small residue of cadmium sulphate was obtained. This could never be totally eliminated from solution by further electrolysis. If this residue is ignored, a slightly lower value for the atomic weight is obtained, but still considerably higher than that of Hulett and his associates. E. H. R.

The Hardness of Metallic Alloys. P. LUDWIK (*Zeitsch. anorg. Chem.*, 1916, **94**, 161—192).—The hardness of a large number of alloys is determined by measuring the penetration of a loaded cone, and is plotted against the "efficacity," the latter being defined as the number of atoms of the dissolved metal in unit volume of the solvent metal. For dilute solid solutions of equal concentration it is expressed in the form $100 . \gamma_A/\alpha_B$, where γ_A is the density of the solvent A and α_B is the atomic weight of the solute B, no chemical compound being formed. In cases in which chemical combination takes place, the expression becomes $\epsilon = 100 . \gamma_A/\alpha_B . (m+n)/n$, where m and n are the respective numbers of the two kinds of atoms in the compound AB. The hardness may then be expected to be proportional to ϵx, where x is the percentage of the added metal by weight.

The experiments have been made with dilute alloys of lead, bismuth, zinc, aluminium, and magnesium in tin; of bismuth, antimony, tin, cadmium, silver, and magnesium in lead; of tin, antimony, aluminium, cadmium, and magnesium in zinc; of lead, silver, zinc, and magnesium in antimony; of bismuth, cadmium, antimony, zinc, tin, silver, copper, and aluminium in magnesium; of tin, silver, zinc, copper, nickel, magnesium, and cobalt in aluminium; and of bismuth, silver, nickel, manganese, antimony, magnesium, zinc, tin, and aluminium in copper, as well as a few ternary alloys.

In most cases the hardness is approximately proportional to the atomic concentration of the solute, the formation of intermetallic compounds being taken into account, but it is by no means independent of the nature of the solute, and many other factors are involved. C. H. D.

New Process for the Preparation of Reactive Lead Peroxide. GEORG PANOPOLUS (*Chem. Zeit.*, 1916, **40**, 339—341).—Compounds of bivalent lead are converted by potassium persulphate into lead sulphate and lead peroxide, the proportions varying according to the temperature and alkalinity of the solutions, higher temperatures and increasing alkalinity favouring the peroxide formation. Both soluble and insoluble salts of lead give products containing but small amounts of peroxide; better results were given by lead oxide, particularly on warming, products containing 35—60% of lead peroxide being isolated. In all cases addition of sodium hydroxide greatly increased the percentage of peroxide in the product, and the best results were obtained by the action of $N/1$

potassium persulphate on a strongly alkaline plumbite solution. The product contained 93·03% of a very active lead peroxide and was free from lead sulphate. G. F. M.

The Equilibrium Diagram of the Mercury-Thallium Alloys. G. D. Roos (*Zeitsch. anorg. Chem.*, 1916, **94**, 358—370).—The diagram determined by Kurnakov and Pushin (A., 1902, ii, 139) shows a maximum on the freezing-point curve corresponding with a compound $HgTl_2$. A repetition of the experiments, with precautions to avoid oxidation, gives the formula of the compound as Hg_5Tl_2, freezing at 14·5°. It forms solid solutions with both mercury and thallium, the series extending from 20 to 31·3 atomic % of thallium. Solid thallium can dissolve up to 18 atomic % of mercury, whilst solid solutions are not formed at the other end of the series. There are two eutectic points, at 9 and 40 atomic % Tl respectively. A molecular transformation of the compound, indicated by development of heat and also by an abrupt discontinuity in the expansion, takes place at 12·8°, this temperature being lowered by the presence of either of the components. C. H. D.

Thallic-thallous Compounds. Alfred Benrath (*Zeitsch. anorg. Chem.*, 1915, **93**, 161—169).—When thallous and thallic bromides are mixed in aqueous solution, the product which separates from concentrated solutions is $TlBr,TlBr_3$, and from dilute solutions $3TlBr,TlBr_3$. The limits of equilibrium at different temperatures have been determined, and are represented on a diagram. The results obtained in the action of light on mixtures of thallic salts and oxalic acid are fully explained as being due to changes in concentration. Ammonium bromide reduces almost as readily as oxalic acid; $2NH_3 + 3TlBr_3 = 3TlBr + 6HBr + N_2$.

The chlorides behave in a similar manner, but concentration has a greater influence than temperature. The reaction

$$3TlCl,TlCl_3 + 2TlCl_3 \rightleftharpoons 3[TlCl,TlCl_3]$$

occurs. The compound $TlCl,TlCl_3$ is white, and not deliquescent.

The compounds $3TlCl,TlCl_3$ and $3TlBr,TlBr_3$ form a continuous series of solid solutions, and the various double salts described by previous authors are not definite compounds.

The thallium nitrates do not form double salts with one another or with the halogen salts.

The only double sulphate which has been obtained is $3Tl_2SO_4,Tl_2(SO_4)_3$, whatever the composition of the original solution. C. H. D.

The Electrolysis of Copper Sulphate Liquors, using Carbon Anodes. Lawrence Addicks (*Trans. Amer. Electrochem. Soc.*, 1915, **28**, 73—110).—In the electrolysis of the solutions obtained in leaching copper ores, graphite anodes may be used with advantage in place of lead or magnetite provided that ferrous sulphate is present as a depolariser. This is more effective than free sulphur dioxide. With too great a current density much

corrosion of the cathode takes place, owing to the action of ferric sulphate on copper. This corrosion increases with rise of temperature. It is almost completely prevented by the presence of a sufficient quantity of aluminium sulphate.

Sulphur dioxide, supplied in a very dilute form as roaster gas, is brought into contact with the solution in a tower. About 0·5 part of sulphur as dioxide is required for one part of copper deposited, and 1019 grams of copper may be recovered per kilowatt-hour. A part of the reduction of ferric sulphate may be brought about by the addition of cement copper, which also removes chlorides. Sulphates are without effect on the deposition, but chlorides contaminate the cathodes. Agitation of the electrolyte is necessary. C. H. D.

Gadolinium Sodium Sulphate. D. W. Bissell and C. James (*J. Amer. Chem. Soc.*, 1916, **38**, 873—875).—A number of bottles containing various amounts of gadolinium and sodium sulphates with 50 c.c. of water were rotated in a thermostat at 25° for several months, and the liquid and solid phases were then analysed. When the amount of sodium sulphate present exceeds that required to form the double salt, the amount of gadolinium sulphate in solution rapidly falls to about 0·6 gram per litre. The composition of the double sulphate appears to be $Gd_2(SO_4)_3,Na_2SO_4,2H_2O$. This is similar to the compound with potassium sulphate according to Benedict. E. H. R.

Gallium-indium Alloy. Philip E. Browning and Horace S. Uhler (*Amer. J. Sci.*, 1916, [iv], **41**, 351—354).—The alloy, found in the form of mercury-like globules on the surface of a residue from the distillation of zinc, contained about 10% of indium with small amounts of zinc and lead and spectrographic traces of copper and silver. It is not readily attacked by the common acids and alkalis, but dissolves readily in aqua regia.

Gallium can be separated from indium by reason of the fact that its hydroxide is soluble in alkali hydroxides in excess; from aluminium, it can be separated by precipitation as ferrocyanide in hydrochloric acid solution. Gallium may also be separated completely from indium electrolytically in alkaline solution. Preliminary experiments also indicate that these two elements may be separated by fractional crystallisation of their ammonium alums.

When the alloy was heated in a vacuum in a silica tube with a blast flame, all the zinc distilled off; at the higher temperature of the oxygen-illuminating gas flame the alloy disintegrated violently, the indium distilling and a globule of nearly pure gallium remaining. The density of the specimen of gallium so obtained was 5·91, the accepted value being 5·95 at 20°. The melting point was 29·5°, and the metal remained liquid when cooled to 0°.

Preliminary results of a spectroscopic examination of gallium, still in progress, are given. A new band spectrum has been observed, the heads of the bands being situated at wave-lengths

3889, 3778, 3677, 3586 (?), 3495, and 3415. Additional lines were also observed at λ 2259, 2294, 2338, 2371, and 2418, but an attempt to discover a hypothetical ultraviolet absorption spectrum of the vapour of the metal failed. E. H. R.

The Oxides of Iron. I. Solid Solution in the System Fe_2O_3–Fe_3O_4. R. B. SOSMAN and J. C. HOSTETTER (*J. Amer. Chem Soc.*, 1916, **38**, 807—833).—In connexion with a study of iron-bearing silicates, it has been found necessary to study the system iron–oxygen with reference to the dissociation pressure of Fe_2O_3. The measurements were made in a vacuum furnace with a platinum-rhodium tube heated by means of an alternating current. The charges of iron oxide were contained in a small platinum crucible, and in this connexion the equilibrium in the system platinum–iron oxide–oxygen is discussed. A considerable part of the paper is devoted to testing the accuracy of the temperature and pressure measurements and their reproducibility.

Ferric oxides from various sources yield practically identical pressures at 1100° and 1200°, excluding certain unexplained minor exceptions. The same pressures are obtained on rising and falling temperatures, and the oxidation of magnetite gives the same result as the dissociation of pure Fe_2O_3. The pressure-composition isotherms at 1100° and 1200° for the system Fe_2O_3–Fe_3O_4 indicate a continuous solid solution series from Fe_2O_3 very nearly to Fe_3O_4. This is also indicated by the fact that the observed pressure depends on the weight of oxide used and the volume of gas space, which was overlooked by earlier observers, and accounts for the uncertainty of their results. No indication of the existence of oxides intermediate between Fe_2O_3 and Fe_3O_4 was found at these temperatures.

An optical examination by H. E. MERWIN confirms the existence of a solid solution, but with more than 18% FeO the opacity of the products prevents further optical confirmation.

The major portion of the oxygen pressure curve at 1200° lies between 4 mm. and 1 mm. The pressure drops rapidly near Fe_3O_4 and rises rapidly near Fe_2O_3. E. H. R.

The Reactions between Cobaltous Oxide and other Metallic Oxides at High Temperatures. J. ARVID HEDVALL (*Zeitsch. anorg. Chem.*, 1915, **93**, 313—319. Compare this vol., ii, 255).—Cobaltous oxide forms regular crystals, whilst those of zinc oxide are hexagonal. Cobaltous oxide may form a hexagonal modification, but the density and colour of the solid solutions of the two oxides do not correspond with the view that this is the form in which the cobalt is present. The properties are better explained by the assumption of a cobalt zincate, which must be green, hexagonal, and of D about 5·4, forming solid solutions with zinc oxide.

Cobaltous oxide does not form any new products with the oxides of copper, calcium, strontium, barium, cadmium, or lead. Glucinum oxide is sometimes stated to give a blue mass with

cobalt, but the product is actually grey, any blue coloration being due to the presence of aluminium. Chromic oxide yields a green mass of the chromite, CoO,Cr_2O_3, which crystallises in octahedra and is very little attacked by acids. Ferric and manganic oxides yield crystalline products, the chemical nature of which has not been determined. A green cobalt vanadate is formed, and a tantalate, which probably has the formula CoO,Ta_2O_5. A crystalline, yellow uranate has been observed. C. H. D.

Chromic Hypophosphite. FR. MAWROW and J. ZONEW (*Zeitsch. anorg. Chem.*, 1915, **93**, 311—312).—A solution of freshly precipitated chromium hydroxide in hypophosphorous acid yields a green mass on evaporation on the water-bath, which may be washed with water and dried over sulphuric acid. Analysis corresponds with the composition $Cr(H_2PO_2)_3,2H_2O$.

Solutions of potassium hypophosphite and chromium alum give first a deposit of potassium sulphate, and the solution yields on further evaporation a gummy mass, from which it has not been possible to obtain a definite salt. C. H. D.

Phosphomolybdic Compounds. III. Complex Hypophosphomolybdenum-semipentoxide-molybdic Acids and their Salts. F. MAWROW and M. NIKOLOW (*Zeitsch. anorg. Chem.*, 1915, **93**, 170—176. Compare A., 1902, ii, 25, 144).—The compound formerly described as $Mo_5O_8,7H_3PO_2,3H_2O$ forms glistening, violet scales and dissolves sparingly in water to a green solution. After being long in contact with water the solid becomes blue and then dissolves to a blue solution. The formula of the violet crystals is $Mo_5O_{13},6H_3PO_2,3H_2O$ or $2Mo_2O_5,MoO_3,6H_3PO_2,3H_2O$.

The blue compound, obtained by boiling the violet compound with water and evaporating the blue solution on the water-bath, is $Mo_5O_{14},6H_3PO_2,4H_2O$ or $Mo_2O_5,3MoO_3,6H_3PO_2,4H_2O$. Its solution gives a blue precipitate with ammonium chloride, having the composition $(NH_4)_2O,Mo_2O_5,5MoO_3,2H_3PO_2,4H_2O$. The sodium salt is $Na_2O,Mo_2O_5,5MoO_3,3H_3PO_2,4H_2O$. Cobaltous chloride also gives a blue precipitate of the composition

$$CoO,Mo_2O_5,5MoO_3,2H_3PO_2,7H_2O.$$

The precipitate with lead nitrate contains admixed lead hypophosphite. C. H. D.

Alkali Double Haloids of Tin and Lead. E. RIMBACH and K. FLECK (*Zeitsch. anorg. Chem.*, 1915, **94**, 139—156).—Ammonium stannous chloride, NH_4SnCl_3,H_2O, is prepared by mixing the components in molecular proportions, allowing the solid phase to separate, saturating with the same mixture while hot, and allowing to cool. It forms needles, and readily loses water. The solubility has been determined over a range of temperature. The potassium salt, $KSnCl_3,H_2O$, forms hair-like crystals and does not lose water until 100°. The corresponding bromides, NH_4SnBr_3,H_2O and $KSnBr_3,H_2O$, are decomposed by water at low temperatures.

Diammonium stannous chloride, $(NH_4)_2SnCl_4$, crystallises with 1 and also with $2H_2O$, the latter being the solid phase in the equilibrium. The potassium salt, K_2SnCl_4, also crystallises with 1 and $2H_2O$. The two bromides, $(NH_4)_2SnBr_4$ and K_2SnBr_4, crystallise with $1H_2O$.

Tetra-ammonium stannous chloride, $(NH_4)_4SnCl_6,H_2O$, and the bromide, $(NH_4)_4SnBr_6,H_2O$, and also the corresponding potassium salts, form stable crystals, all of which contain $1H_2O$.

Tetra-ammonium lead chloride, $(NH_4)_4PbCl_6,H_2O$, has been prepared, but potassium and rubidium only yield the salts $KPbCl_3$ and $RbPb_2Cl_5$ respectively. C. H. D.

Hetero-poly-acids containing Vanadium. V. Compounds which contain Molybdic and Selenious Acids. WILHELM PRANDTL and W. VON BLOCHIN (*Zeitsch. anorg. Chem.*, 1915, **93**, 45—74. Compare A., 1915, ii, 469).—Physicochemical methods fail to indicate the constitution of the hetero-poly-salts, and the authors have therefore aimed at applying the method of substitution, borrowed from organic chemistry.

Hexavanadates form definite compounds with selenites and with molybdates. The replacement of the one acid by the other should therefore be possible. The salts containing only molybdenum and selenium, without vanadium, have first been examined.

The salt $2(NH_4)_2O,2SeO_2,5MoO_3,3H_2O$ is formed when concentrated ammoniacal molybdenum solutions and ammonium selenite are acidified and rapidly crystallised. It is readily soluble in water, and forms small, rhombic prisms. Water slowly converts it into the compound $3(NH_4)_2O,2SeO_2,8MoO_3,6H_2O$. A basic salt has also been obtained.

The potassium salt, $2K_2O,2SeO_2,5MoO_3,2$ or $5H_2O$, is stable, both hydrates being obtained in crystals. The rubidium salt also crystallises with 2 and $5H_2O$, both hydrates being monoclinic. Crystallographic data [by H. STEINMETZ] are given. The lithium and sodium salts are too soluble to be isolated. The barium salt crystallises with 7 and $10H_2O$, the pentahydrate being rhombic.

Slow crystallisation of the ammonium salt at high temperatures gives the salt $3(NH_4)_2O,2SeO_2,8MoO_3,5$ and $6H_2O$. The corresponding potassium salt has not been obtained. Barium chloride precipitates a solution of the 2 : 8 salt, yielding

$$3BaO,2SeO_2,8MoO_3,10H_2O.$$

It has not been found possible to replace more than two MoO_3 groups in ammonium paramolybdate by selenious acid.

[With HEINZ OBPACHER.]—Solutions of ammonium molybdate and selenite are precipitated hot by concentrated nitric acid, and then yield yellow, uncrystallisable precipitates resembling the phosphomolybdates, and containing $2SeO_2 : 12MoO_3$. The precipitation is not quantitative. By boiling and adding nitric acid very gradually, the compounds $2(NH_4)_2O,6SeO_2,6MoO_3,9H_2O$, $2(NH_4)_2O,7SeO_2,6MoO_3,8H_2O$, $2(NH_4)_2O,2SeO_2,5MoO_3,3H_2O$, and $2(NH_4)_2O,2SeO_2,12MoO_3,13H_2O$ have been obtained. C. H. D.

Iso- and Hetero-poly-acids. XII. The Determination of the Constitution of Hetero-poly-acids. ARTHUR ROSENHEIM (*Zeitsch. anorg. Chem.*, 1915, **93**, 273—286).—A criticism of the views of Prandtl (preceding abstract). Analytical methods are insufficient to determine the constitution of the salts of hetero-poly-acids, and the assumption of alkali hydrogen molybdates and similar salts is contrary to the physicochemical facts, which show that such salts, like alkali hydrogen chromates, are incapable of existence. Moreover, many of the compounds described by Prandtl are undoubtedly isomorphous mixtures of salts. It is quite possible, contrary to the statement of Prandtl, to distinguish between the water of crystallisation and water of constitution by measurements of the loss of water at different temperatures.

[With E. BRAUER.]—Determinations of the hydrogen ion concentration in solutions of metatungstic acid and substituted acids containing boron, silicon, and phosphorus show that these acids are of practically equal strength, and are somewhat stronger than phosphoric acid. C. H. D.

Subhaloid Compounds of Some Elements. V. and VI. So-called Bismuth Subchloride. L. MARINO and R. BECARELLI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 221—227, 326—331. Compare this vol., ii, 190).—The system bismuth–bismuth tribromide has been studied in the manner previously employed. Solidification of the fused mixtures lying within definite limits of concentration yields two layers, the upper one consisting of black, acicular crystals and the lower one of a mass of crystals with metallic lustre, m. p. 230—270°, and covered with a black skin; the lower crystals are sensitive to light, and soon lose their brilliancy and become iridescent and then greyish-blue. The black upper layer does not consist of a single compound, but is separable into a highly hygroscopic black mass and a crystalline network melting over a range of temperature above 270°.

No subchloride is here formed (compare Eggink, A., 1908, ii, 1043), the fused mixtures of bismuth and its trichloride yielding, over a certain interval of concentration, a series of mixed crystals (α), which undergo transformation, accompanied by marked development of heat, into β-crystals with melting points higher in all cases than those of bismuth and its trichloride. After complete fusion the β-crystals yield, on cooling, α-crystals of different composition in presence of two liquid layers which reproduce the same phenomena. T. H. P.

Mineralogical Chemistry.

Molten Silicic Acid as Mineral (Lechatelierite). A. LACROIX (*Chem. Zentr.*, 1916, **1**, 456; from *Bull. Soc. franç. Min.*, 1915, **38**, 182—186).—The mineralogical designation of molten silicic acid as fulgurites is considered inappropriate, and the name lechatelierite is suggested. The following data for molten silicic acid are recorded: D 2·204, n_D 1·458477, hardness 5·5.

H. M. D.

The Chemical Structure of the Tertiary Potash Deposits of Upper Alsace. M. RÓZSA (*Zeitsch. anorg. Chem.*, 1915, **93**, 137—150).—Deposits rich in halite and sylvite respectively alternate throughout the deposits. Kainite and kieserite are absent. The arrangement is consistent with the view that the deposits are formed by the discontinuous evaporation of mixed solutions, consisting of various fractions and mother liquors from sea-water, together with fresh water. The periodicity is attributed to alternations of temperature. In many parts alternations of clay and dolomite-anhydrite occur, indicating the periodical inflow of dilute solutions. The primary carnallite has in places undergone secondary conversion to sylvite. C. H. D.

The Quantitative Relations of the Hydrothermal Transformations of the Principal Salts in the Stassfurt Potash Deposits. M. RÓZSA (*Zeitsch. anorg. Chem.*, 1915, **94**, 92—94. Compare A., 1915, ii, 257).—Analyses of certain layers, which are tabulated, show that the hydrothermal transformations take place without the formation of an intermediate product, kainite. This is not invariably the case. C. H. D.

Minerals of the Metalliferous Deposit of Borgofranco d'Ivrea. G. LINCIO (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 227—230).—The nodular masses of native arsenic occurring in the metalliferous deposit of Borgofranco contain occasional interposed strata of a lead-grey mineral composed of fine fibres normal to the surfaces of the enclosing strata. Its composition is

As.	As_2O_3.	Sb.	Pb.	Ag.	Cu.	Fe.	S.	Total.
90·91	5·23	1·03	1·02	0·83	0·12	0·07	0·74	99·95

and it appears to be a native antimoniferous arsenic, through which are ramified silver and a little copper, possibly as metals; the arsenic trioxide, lead sulphide, sulphur, and iron are regarded as impurities. T. H. P.

A New Mineral (Furnacite) from the Middle Congo (French Equatorial Africa). A. LACROIX (*Chem. Zentr.*, 1916, i, 485—486; from *Bull. Soc. franç. Min.*, 1915, **38**, 198—200).—The mineral described was discovered in a vein of dioptase. It has a deep olive

green colour, is apparently monoclinic, and melts to form a dark green glass. It contains arsenic, chromium, copper, and lead, and is supposed to be a basic chromoarsenate of lead and copper analogous to vauquelinite, the thermophosphate of the same metals.

H. M. D.

Malacone from the Pegmatites of Madagascar. A. LACROIX (*Chem. Zentr.*, 1916, i, 486; from *Bull. Soc. franç. Min.*, 1915, **38**, 200—204).—The occurrence of malacone (D 3·62) in the pegmatites of Madagascar is recorded. Analysis of (1) a brownish-red malacone from Ambolotora, and (2) a light brown malacone from Ambatolampikely, gave:

	SiO_2.	ZrO_2.	ThO_2.	Cb_2O_5.	Al_2O_3.	Fe_2O_3.	Na_2O.	H_2O.	Total.
(1)	17·4	52·2	0·8	8·0	5·6	3·1	—	9·5	101·6
(2)	18·1	59·9	1·16	6·6	2·32	2·72	0·2	9·5	100·5

The columbium pentoxide is considered to represent a foreign ingredient and not a normal constituent of the mineral.

H. M. D.

Manandonite and Cookeite. A. LACROIX (*Chem. Zentr.*, 1916, i, 485; from *Bull. Soc. franç. Min.*, 1915, **38**, 142—146).—Analyses of manandonite gave the following results:

SiO_2.	Al_2O_3.	B_2O_3.	MgO.	Na_2O.	K_2O.	Li_2O.	H_2O.	Total.
25·20	49·20	6·95	0·11	0·40	0·31	3·75	15·50	100·42

which show that this mineral differs chemically from cookeite. Both are formed by the decomposition of lithium-containing minerals.

H. M. D.

Dioptase from Cordoba, Argentina. E. QUERCIGH (*Jahrb. Min.*, 1916, i, Ref. 159—161; from *Rend. Accad. Sci. Fis. Mat. Napoli*, 1914, 12 pp.).—Radial aggregates of crystals occur with quartz crystals and some limonite and malachite in drusy cavities in quartzite at Chiviquin, prov. Cordoba. D^{18} 3·307. Curves plotting the refractive indices show a weak anomalous dispersion in the green. Analysis shows the material to be very pure H_2CuSiO_4. The water is expelled below red heat.

SiO_2.	CuO.	Fe_2O_3.	H_2O.	Total.
38·15	50·26	0·09.	11·31	99·81

L. J. S.

The Pure Kieselfulgurites of the Eastern Sahara and certain Silicious Fulgurites of the Pyrenees. A. LACROIX (*Chem. Zentr.*, 1916, i, 457; from *Bull. Soc. franç. Min.*, 1915, **38**, 188—198).—The structure of the fulgurites is described. On treatment with hydrofluoric acid, 1—5% residue is obtained containing aluminium, iron, calcium, and alkalis. They are to be regarded as impure varieties of lechatelierite.

H. M. D.

The Manganese in some Springs Rising in the Central Mountains and in some Stations on the Plain of Languedoc. F. JADIN and A. ASTRUC (*Compt. rend.*, 1916, **162**, 643—645. Compare this vol., ii, 145).—The authors have determined the

manganese content of the waters of nine springs in the Montagne Noire at the south-west end of the Central Plateau and of ten springs in the plain of Languedoc. The results obtained for the mountain springs confirm the conclusions already noted (*loc. cit.*), but the waters of the plain of Languedoc do not, on the whole, show sufficient homogeneity to allow of their being placed in a sharply defined group. W. G.

Analytical Chemistry.

A Possible Source of Error in Colorimetric Observations J. H. LONG (*J. Amer. Chem. Soc.*, 1916, **38**, 716—718).—The author traced discrepancies in a series of readings with his Duboscq colorimeter to the fact that the prisms are set in a wax which does not maintain its rigidity if the instrument is used in a hot place. J. C. W.

Indicators from Animal Tissues. W. J. CROZIER (*J. Biol. Chem.*, 1916, **24**, 443—445).—A pigment is extracted by acetone from the test of the common black tunicate of Bermuda and the West Indies (*Ascidia atra*), the solutions of which are turned red by acids and green by alkalis. The transition point is at about $p_H = 7{\cdot}5$.

The integument of the orange-red annelid *Eupolymnia aurantiaca* when extracted with aqueous alcohol yields a bright red solution which turns green at $p_H = 10{\cdot}0$.

The indicator contained in the nudibranch *Chromodoris zebra* has already been described (A., 1914, i, 454). H. W. B.

Potassium Dichromate as a Standard. I. G. BRUHNS (*J. pr. Chem.*, 1916, [ii], **93**, 73—105).—On account of the ease with which it can be purified and its stability, potassium dichromate has many advantages as a volumetric standard, but Zulkowski and Wagner, amongst others, state that it has a high titration value, amounting to 0·3% to 0·45% in excess of its true equivalent. When their calculations are corrected by the introduction of present-day atomic weights, part, but not all, of the discrepancy disappears. Wagner supposed that dichromate may catalytically promote oxidation by means of dissolved oxygen, and appear therefore to have a higher titration value, but as potassium chromate, iodate, and other allied reagents show no such abnormality, this explanation is considered improbable.

Different samples of carefully purified potassium dichromate were titrated against potassium iodide–sodium thiosulphate and against ferrous sulphate for comparison with potassium permanganate, and

gave very concordant results, no such differences as those observed by Wagner being found. The ratio between dichromate and permanganate was exactly the same whether they were compared by means of sodium thiosulphate or ferrous sulphate, and the conclusion is drawn that the oxidation processes follow the same course with both oxidising agents.

Although potassium dichromate can be accurately titrated as an acid against potassium hydroxide with phenolphthalein as indicator, it is found that the acidity of the solution increases with concentration. The solution is therefore of no value for use as a standard acid.

Potassium dichromate can best be standardised gravimetrically by means of carefully purified oxalic acid, which in point of purity can be compared with sodium chloride. Oxalic acid, too, links up the oxidising reagents with acids. Since the oxidation of oxalic acid by dichromate does not go smoothly, comparison of the two must be made through ferrous sulphate and potassium permanganate. Careful experiments showed that 100 c.c. $N/10$ potassium dichromate = 100·14 c.c. $N/10$ oxalic acid. Compared with sodium chloride, oxalic acid has been shown to be 0·01% too strong. Potassium dichromate is therefore 0·13% too strong instead of 0·2—0·3%, as asserted by Wagner. It is held that this high titration value is not a specific property of the salt, but one depending in an important degree on the different tests applied.

An appendix deals with the direct comparison of dichromate and permanganate solutions which is to be carried out with ferrous sulphate. When the two solutions are approximately equivalent, it is recommended to measure out slightly less than the necessary volume of dichromate with a pipette, and to finish off with permanganate from a burette. After a little practice the green colour of the chromium salt does not interfere with the observation of the end-point in day- or lamp-light. The sharpness of the end-point can be increased by the addition of phosphoric acid or cobalt sulphate, or the use of a little potassium ferricyanide insufficient to form a precipitate.

For the preservation of permanganate solutions, pure materials, clean apparatus, and protection from organic dirt are the chief essentials. The solution should be decanted from any manganese dioxide which may have formed after preparation, but this takes a very long time to settle. E. H. R.

General Applicability of the Paper Pulp Filter to Quantitative Analysis. S. L. Jodidi and E. H. Kellogg (*J. Ind. Eng. Chem.*, 1916, **8**, 317—319).—A filter prepared by disintegrating ordinary filter paper with water and collecting the emulsion in a Gooch crucible yields very satisfactory results when used for the collection of precipitates, such as barium sulphate, silver chloride, potassium platinichloride, etc. W. P. S.

Detection and Estimation of Halogens in Organic Compounds. I. Drogin and M. A. Rosanoff (*J. Amer. Chem. Soc.*, 1916, **38**, 711—716).—The authors have investigated the condi-

tions necessary for obtaining trustworthy results in the estimation of halogens by the Stepanoff-Bacon method. Full details are given of the procedure which they recommend, the important point being that they use about 10% more sodium than did Bacon.

J. C. W.

Estimation of Iodine and Bromine in Saline Waters from Petroleum-bearing Strata. D. E. Popa (*Bull. sci. Acad. Roumaine*, 1915—16, **4**, 308—317).—A modification of a method proposed by Weszelszky (A., 1900, ii, 436) is recommended; the method depends on the oxidation of the iodine to iodic acid by means of chlorine in acid solution, the bromine at the same time being liberated and removed by distillation. A small quantity of bromine is, however, converted into bromic acid, and the modification described consists in a double treatment with chlorine, with intervening reduction, in order to recover all the bromine. One hundred c.c. of the water are rendered alkaline with sodium hydroxide, evaporated, the residue is ignited at a low temperature in order to destroy organic substances, then dissolved in water, the solution filtered, and the insoluble portion washed. The filtrate and washings are evaporated to about 70 c.c., transferred to a distillation flask, and acidified with sulphuric acid or hydrochloric acid. Seventy-five c.c. of 1% chlorine water are now added, the flask is connected with a receiver containing 1% potassium hydroxide solution, and the contents of the flask are heated, a current of carbon dioxide being passed through the apparatus when steam begins to enter the receiver. After continuing the distillation for about thirty minutes, the contents of the flask are cooled, 20 c.c. of saturated sulphur dioxide solution (at 0°) are added, and the mixture is boiled until practically all the sulphur dioxide has been expelled; the receiver is meanwhile detached, the alkaline solution transferred to a porcelain dish, and a fresh portion of potassium hydroxide solution introduced. The solution in the flask is then treated with chlorine and the distillation repeated. The united distillates are evaporated, the residue is heated on a boiling water-bath for forty-five minutes, then dissolved in 130 c.c. of water, the solution treated with potassium iodide and sulphuric acid, and the liberated iodine titrated in the usual way; its quantity is a measure of the amount of bromine present. The solution remaining in the distillation flask is boiled for about fifteen minutes to remove a small trace of bromine which remains (this amount of bromine is too small to affect the result for bromine, but interferes with the iodine estimation), then cooled, potassium iodide is added, and the liberated iodine titrated.

W. P. S.

Titration of Iodine and Iodides with Arsenious Acid. A. Thiel and E. Meyer (*Zeitsch. anal. Chem.*, 1916, **55**, 177—185).—The method described by Müller and Wegelin (A., 1914, ii, 67) is trustworthy provided that the hydrogen ion concentration of the solution to be titrated lies between the limits $10^{-6 \cdot 5}$ and $10^{-7 \cdot 5}$. Borates, or a mixture of phosphates, should be used

in place of sodium hydrogen carbonate for reducing the acidity of the solution (compare Washburn, A., 1908, ii, 363). W. P. S.

Analysis of Lime–Sulphur Solutions. II. Estimation of "Poly-sulphur." ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1916, **8**, 339—341. Compare this vol., ii, 262).—The reaction

$$Ca(m-S)(p-S)_y + yNa_2SO_3 = CaS + yNa_2S_2O_3$$

is the basis of the method proposed. The monosulphide is removed as zinc sulphide, the excess of sulphite as strontium sulphite, and the thiosulphate is then titrated with iodine solution; a correction is made for the thiosulphate present originally in the lime–sulphur solution. Ten c.c. of a diluted portion of the sample, containing about 2% of sulphide sulphur, are heated on a boiling water-bath for fifteen minutes with 10 c.c. of 10% sodium sulphite solution, 20 c.c. of $N/5$ ammoniacal zinc chloride solution, and 25 c.c. of water. Twenty-five c.c. of water are then added, the heating is continued for a further thirty minutes, and the mixture treated with 20 c.c. of 10% strontium chloride solution. After cooling for five minutes, the mixture is filtered, the precipitate washed, the filtrate treated with 1 c.c. of 10% disodium phosphate solution, then diluted to 250 c.c., and filtered. Two hundred c.c. of the filtrate are rendered slightly acid with tartaric acid solution, using methyl-red as indicator, and then titrated with $N/10$ iodine solution. After subtracting 0·1 c.c. from the number of c.c. of iodine solution used, the remainder is multiplied by 1·25, and the thiosulphate number (*loc. cit.*) is deducted from the result in order to obtain the "poly-sulphur" number. The latter multiplied by 0·03207 gives the percentage of "poly-sulphur" in the sample; the sulphide-acid number multiplied by 0·016035 gives the percentage of mono-sulphur, and the thiosulphate number multiplied by 0·06414 the percentage of thiosulphate-sulphur. W. P. S.

Accurate End-point in the Volumetric Estimation of Sulphur in Steel. HERBERT ZSCHIEGNER (*J. Ind. Eng. Chem.*, 1916, **8**, 324).—Whilst the method depends on the production of starch-iodide, the actual blue colour of the latter is disregarded in determining the end-point of the sulphide titration. The titration is carried out in a white porcelain beaker on the bottom of which is cemented a small disk of black celluloid. The estimation is proceeded with as usual up to the commencement of the titration; the iodine solution is added slowly when the mixture begins to darken, and the end-point is denoted when the addition of a further drop of iodine solution renders the black disk invisible. The volume of the hydrochloric acid used to decompose the cadmium sulphide, the volume of the starch solution added, and the volume of the final solution must be equal to the volumes of the solutions used in standardising the iodine solution.
W. P. S.

Innovations in the Analysis of Potable Waters. TORQUATO GIGLI (*Ann. Chim. Applicata*, 1916, **5**, 75—82).—For the rapid

examination of a number of samples of drinking water and the detection of small changes in them, the author tests qualitatively for nitrites, nitrates, ammonium compounds and sulphates, and estimates the total hardness by the soap method, the chlorine by Mohr's method, the temporary and the permanent alkalinity and the temporary and the permanent electrical resistance. The permanent alkalinity is determined by boiling 100 c.c. of the water for twelve minutes in a reflux apparatus, filtering the cold water, washing the precipitate with a little cold, boiled distilled water, and titrating with 0·05*N* hydrochloric acid in presence of methyl-orange; the small amount of alkalinity extracted from the glass by the boiling water is corrected for by means of a similar test with distilled water. The permanent alkalinity gives a measure of the carbonates not precipitated by boiling, that is, of the magnesium carbonate and the carbonates of the alkali metals. The temporary alkalinity, representing the temporary hardness, does not agree well with the value of the latter given by the soap test, the latter yielding uncertain results owing to the slowness with which the magnesium salts react with the soap.

The "permanent resistance" is determined after the water has been boiled and filtered, and differs from the original resistance by an amount corresponding with the calcium carbonate deposited. Calculation of the calcium carbonate in this way by means of the expression, residue = 686888/resistance, gives a value lower than the temporary alkalinity, owing to the glass dissolved by the water during boiling. T. H. P.

A Comparative Study of Aeration and Heat Distillation in the Kjeldahl Method for the Estimation of Nitrogen. K. GEORGE FALK and KANEMATSU SUGIURA (*J. Amer. Chem. Soc.*, 1916, **38**, 916—921).—Kober's method (compare A., 1908, ii, 776; 1910, ii, 651; 1913, ii, 978) for the distillation of the ammonia after digestion with acid in the Kjeldahl method of estimating nitrogen was tested with a number of substances and found to be untrustworthy, as in every case varying amounts of ammonia were found to have been left in the solution and could only be removed by the ordinary heat distillation. W. G.

Estimation of Nitrogen by Kjeldahl's Method. II. OTTO NOLTE (*Zeitsch. anal. Chem.*, 1916, **55**, 185—189. Compare A., 1915, ii, 482).—Too low results are obtained in the estimation of nitrogen in caffeine and uric acid if mercury (13 grams) is added during the acid digestion; loss of nitrogen also takes place when ammonium sulphate is digested with sulphuric acid in the presence of mercury, but mercuric sulphate has no influence on the estimation of nitrogen in ammonium sulphate by direct distillation. If the mercury is replaced by copper foil, loss of nitrogen also takes place during the acid digestion of caffeine, uric acid, and silver cyanide; in the case of silver cyanate and trimethylamine hydrochloride, the presence of copper accelerates the formation of ammonia, but has a retarding action in the acid digestion of methylindole. W. P. S.

Approximate Estimation of Nitrates in Water in the Presence of Nitrites. L. von Liebermann and D. Acél (*Chem. Zentr.*, 1916, i, 266—267; from *Hyg. Rdsch.*, 1915, **25**, 805—808).—The nitrates are reduced to nitrites by means of zinc and acetic acid, and the nitrite is estimated colorimetrically with the Griess-Ilosvay reagent. Nitrites, if present in the water, are removed previously by treatment with urea. W. P. S.

Estimation of Phosphoric Acid by the Citro-Uranium Method. D. Crispo and R. W. Tuinzing (*Landw. Versuchs-Stat.*, 1916, **88**, 131—141).—The citrate soluble phosphoric acid in phosphatic fertilisers may be estimated by precipitating the phosphoric acid as ammonium magnesium phosphate under the conditions described by Popp (A., 1912, ii, 992), dissolving this precipitate in hot acetic acid, and titrating the solution with standardised uranium acetate solution, using potassium ferrocyanide as the indicator. For the estimation of total phosphoric acid in fertilisers containing much silica, it is found that the interfering action of the latter may be eliminated by boiling 10 grams of the sample with 5 grams of ferrous sulphate and filtering the mixture. Results of numerous estimations of phosphoric acid in a variety of fertilisers are recorded, showing that the results obtained by the method are trustworthy. W. P. S.

Estimation of Citrate Soluble Phosphoric Acid in Basic Slag by the Iron Citrate Method. Celichowski and Ferd. Pilz (*Chem. Zentr.*, 1916, i, 79; from *Zeitsch. landw. Vers.-Wesen Oesterr.*, 1915, **18**, 581—591).—Fresh, undecomposed ferric chloride, which gives a clear solution, must be employed, and the solution of hydrogen peroxide should not be kept too long and its strength should be ascertained from time to time. Iron citrate should be added first to the citric acid extract, then hydrogen peroxide, and last magnesia mixture, the solution being stirred to expedite the precipitation. N. H. J. M.

Estimation of Citrate Soluble Phosphoric Acid by the Iron Citrate Method. M. Popp (*Chem. Zentr.*, 1916, i, 79; from *Zeitsch. landw. Vers.-Wesen Oesterr.*, 1915, **18**, 592—594).—The paper of Zacharides and Czak (*ibid.*, 472) is discussed. N. H. J. M.

Reduction of Arsenic Compounds to Arsenious Compounds and the Estimation of Arsenic by Distillation as Arsenic Trichloride. R. C. Roark and C. C. McDonnell (*J. Ind. Eng. Chem.*, 1916, **8**, 327—331).—It is shown that ferrous salts do not effect complete reduction of arsenic compounds in hydrochloric acid solution, and that in those cases where trustworthy results have been obtained by the distillation method, using ferrous salts as reducing substances, one or more of the following conditions must have obtained: metallic copper or a copper salt was present, in which case some cuprous chloride would be formed; the arsenic was present in very small amount; or the arsenic was present as

metallic arsenic or arsenite, and not as arsenate. Cuprous chloride reduces arsenic compounds quantitatively, and the arsenic chloride may be separated completely by distillation from antimony, lead, copper, zinc, iron, and calcium salts. W. P. S.

Estimation of Carbon in Steels and Irons by Direct Combustion in Oxygen at High Temperature. J. R. CAIN and H. E. CLEAVES (*J. Ind. Eng. Chem.*, 1916, **8**, 321—324. Compare A., 1914, ii, 816).—The additional quantity of carbon obtained by increasing the temperature to above the fusing point of the oxides after the metal has been burnt in oxygen in the usual way does not exceed 0·02%, and in the greater number of cases is not more than 0·01%. The ordinary method of carrying out the combustion is therefore sufficiently trustworthy. W. P. S.

New Form of Absorption Bottle for Use with Calcium Chloride or Soda Lime in the Elementary Analysis of Carbon and Hydrogen in Organic Substances. HARRY L. FISHER (*J. Ind. Eng. Chem.*, 1916, **8**, 368—369).—A bottle has an inner tube fused to its bottom, and a single, ground-in stopper makes an air-tight joint with the neck of the bottle and the top of the inner tube. The inlet and outlet tubes for the gas enter the side of the neck of the bottle, one connecting with the inner tube through a hole in the stopper or a short tube in the latter, and the other with the space between the inner tube and the bottle itself. Small holes at the bottom of the inner tube allow the gas to pass from the latter to the outer space and thence to the exit tube, or vice versa. The calcium chloride, etc., is filled into the inner tube and into the space between this and the sides of the bottle.
W. P. S.

Direct Estimation of Carbon Monoxide in Mixtures containing Unsaturated Hydrocarbons. A. PIVA (*Ann. Chim. Applicata*, 1916, **5**, 82—93. Compare A., 1915, ii, 447).—The absorption of carbon monoxide by alkali hydroxide, with formation of the corresponding formate, proceeds rapidly and quantitatively at 200—240°, and has its maximum velocity at about 230°. On the other hand, the secondary reactions expressed by the equations $2H\cdot CO_2M = M_2CO_3 + H_2 + CO$ and $2H\cdot CO_2M = C_2O_4M_2 + H_2$ commence only above 240°. On these observations the author bases a method for the estimation of carbon monoxide in presence of unsaturated hydrocarbons. Prior to the absorption of the carbon monoxide, the oxygen is removed from the apparatus by means of alkaline pyrogallol or sodium hyposulphite solution. The absorption is then effected by means of moderately fine soda lime containing about 20% of sodium hydroxide and placed in a semicircular tube heated at 230° in a copper cylinder furnished with an asbestos cover. The treatment of the gas with the soda lime is repeated until no further diminution in volume occurs. The method gives satisfactory results for the estimation of carbon monoxide in (1) mixtures containing (*a*) oxygen and nitrogen, (*b*) nitrogen, (*c*) nitrogen

and ethylene, or (*d*) nitrogen and acetylene, or (2) illuminating gas, (3) Dowson gas, or (4) gas formed by the decomposition of barium formate at 500—600° or calcium formate at 400°.

T. H. P.

The Qualitative Separation of Silver from Univalent Mercury. N. von Zweigbergk (*Zeitsch. anorg. Chem.*, 1916, **93**, 320—326).—In the ordinary separation of silver chloride from mercurous chloride by means of ammonia, a part of the silver is always retained by the black precipitate, and when the quantity of silver is relatively small it may be overlooked entirely. The silver is retained in the form of an amalgam, this being an additional proof that the black precipitate consists of a mixture of the mercuric compound and metallic mercury.

The mixture of chlorides should be oxidised by means of bromine or of sodium hypochlorite and nitric acid to convert mercury to the mercuric condition.

C. H. D.

Determination of the Hardness of Natural Waters, and the Use of Methyl-red as an Indicator. Sydney A. Kay and Susan H. Newlands (*J. Soc. Chem. Ind.*, 1916, **35**, 445—447).—A rough relationship is traceable between electrical conductivity and hardness of natural waters, twenty units (gemmhos) of conductivity corresponding with about one degree of hardness. In the estimation of temporary hardness by Hehner's method, methyl-red is a more suitable indicator than methyl-orange. Yellow in neutral solution, it changes to red at $H=10^{-5}$, and is therefore ten times as sensitive as methyl-orange. For this reason it is, of course, necessary to remove carbon dioxide from the solution during the titration either by boiling or by passing a current of air. Incidentally the authors point out the advantage of using methyl-red for all purposes, particularly for ammonia titrations, and titrations by artificial light. In the estimation of permanent hardness, the inaccuracies attendant on the sodium carbonate evaporation method are obviated by evaporating the water with a known excess of potassium carbonate in a platinum basin, extracting with 20% alcohol, and titrating the filtrate and washings, after rinsing out the basin with 90% alcohol, with $N/50$-hydrochloric acid, using methyl-red as indicator. The total hardness may then be obtained either by a titration of the carbonate precipitate remaining from the above operation, or by repeating the experiment as for the determination of permanent hardness, after first neutralising the water as in determining temporary hardness. The potassium carbonate required to precipitate the calcium and magnesium salts is then equivalent to the total hardness. In carrying out the above methods, contamination of the contents of evaporating basins with oxides of sulphur, etc., from coal gas flames must be guarded against, and the use of soft glass vessels for the titrations may also lead to serious error. Taking such precautions the error rarely exceeds 0·2 degree.

G. F. M.

Estimation of Calcium and Magnesium in Natural Waters. SYDNEY A. KAY and SUSAN H. NEWLANDS (*J. Soc. Chem. Ind.*, 1916, **35**, 447—449).—A rapid method for the individual estimation of calcium and magnesium in natural waters is based on the fact that calcium carbonate is practically insoluble in ammonium carbonate, whilst magnesium carbonate is soluble in an excess of that reagent. One hundred c.c. of the water are evaporated to dryness in a platinum dish with 10 c.c. of 2% ammonium carbonate solution. The residue is extracted three times with 15 c.c. of ammonium carbonate solution on a water-bath and the final residue washed four times with 90% alcohol until the washings are free from alkalinity. The residue of calcium carbonate is dissolved in *N*/10-hydrochloric acid and titrated back with *N*/50-baryta solution. The difference between the calcium as thus found and the total hardness as determined by the method described in the previous abstract gives the magnesium. G. F. M.

A Study of Indicators for the Determination of Temporary Hardness in Water. JOHN F. NORTON and H. I. KNOWLES (*J. Amer. Chem. Soc.*, 1916, **38**, 877—884).—Starting from the principle that in any titration with a given indicator, the end-point, determined by colour-change, is reached when the hydrogen ion concentration attains a definite value depending on the ionisation constant of the indicator and the fraction transformed, experiments have been made to determine the most suitable indicator for use in titrating natural waters. A series of waters was prepared containing known amounts of calcium and magnesium hydrogen carbonates, calcium chloride, and magnesium sulphate, and these were titrated with acid in presence of indicators chosen from among those which change colour between hydrogen ion concentrations of 10^{-4} and 10^{-6}. A suitable end-point colour for each indicator had been previously determined. Butter-yellow (dimethylaminoazobenzene) gave the best results, methyl-orange, methyl-red, and sodium alizarinsulphonate giving low results, whilst lacmoid and phenacetolin gave end-points varying according to the heat treatment of the solution. In presence of alum, lacmoid gives the best results. A standard colour is recommended for titrations with butter-yellow. E. H. R.

Rapid Assay of Lead. GREGORY TOROSSIAN (*J. Ind. Eng. Chem.*, 1916, **8**, 331).—About 0·2 gram of the finely-powdered sample (lead oxide, lead sulphate, red lead, etc.) is placed in a shallow depression in an aluminium plate (made by placing a piece of aluminium plate over a hole and striking it with a pestle) and then moistened with a few drops of dilute hydrochloric acid. More of the acid is added gradually until the lead has been reduced completely; this usually takes from five to ten minutes. The spongy lead is then washed with water, pressed with a glass rod into a compact mass, dried, and weighed. The results obtained do not generally differ by more than 0·2% from those found by the ordinary methods. W. P. S.

A Rapid Method for the Estimation of Copper and Iron. GRAHAM EDGAR (*J. Amer. Chem. Soc.*, 1916, **38**, 884—887).—A modification of Volhard's method for the estimation of copper is suggested by which copper and iron may both be estimated in the same solution. The solution containing some sulphuric acid is nearly neutralised with ammonia or sodium carbonate, and a known volume of standard ammonium thiocyanate solution is added sufficient to precipitate all the copper, the solution being at the same time boiled and saturated with sulphur dioxide so that the iron is completely reduced. A current of carbon dioxide is now passed and the solution boiled to remove SO_2, after which it is cooled and filtered. The filtrate is treated with excess of standard silver nitrate solution, and the iron is then titrated with standard permanganate solution. A trace of ferrous sulphate is added to decolorise the permanganate, and the excess of silver nitrate is titrated with standard thiocyanate. From the total thiocyanate and silver nitrate used the copper can then be calculated. The method gives accurate results and is well adapted to the analysis of ores. E. H. R.

Alkalimetric Estimation of Certain Bivalent Metals in the Form of Tertiary Phosphates, with Especial Reference to the Volumetric Estimation of Cobalt and Nickel. W. R. SCHOELLER and A. R. POWELL (*Analyst*, 1916, **41**, 124—130).—The volumetric estimation of certain metals which yield phosphates of the type $M''NH_4PO_4$ was investigated. Ammonium magnesium phosphate, after being washed with ammonia solution and then with 50% alcohol to remove free ammonia, may be titrated with $N/10$-acid solution, using cochineal as indicator. Zinc, cadmium, and manganese can also be titrated after precipitation as phosphate. The following process is recommended for the estimation of cobalt. The cobalt solution (which may also contain nickel) is treated with an amount of ammonium phosphate equal to five times the combined weights of the cobalt and nickel, and dilute ammonia is added, drop by drop, to the boiling solution until the blue precipitate at first formed becomes pink. The precipitate is then collected, washed, rinsed into a beaker, and titrated with standard acid until the precipitate disappears; an indicator is not required. A double precipitation of the cobalt is necessary to remove all the nickel if this metal is present. The nickel in the slightly ammoniacal filtrate from the cobalt phosphate may be titrated with cyanide solution without further manipulation; this titration should be made without delay, as a precipitate tends to form after a time. W. P. S.

New Methods of Testing for Molybdenum. JAMES MOIR (*J. Chem. Metall. Min. Soc. S. Africa*, 1916, **16**, 191—192).—An alkali molybdate solution, when acidified with acetic acid and treated with a small quantity of hydrazine or quinol, and boiled, yields a deep blue coloration. A slightly acid solution of molybdic acid also yields a blue coloration when boiled for some time with

the addition of potassium iodide. A sensitive test for molybdenum is reduction with zinc in the presence of a thiocyanate; a crimson coloration is obtained. If iron is also present, a red coloration is obtained on adding the thiocyanate, but the colour disappears on reduction and the crimson coloration due to the molybdenum then develops. An orange coloration is obtained when molybdic acid in acetic acid solution is treated with pyrogallol or pyrocatechol. W. P. S.

Estimation of Vanadium by "Cupferron" (Ammonium Nitrosophenylhydroxylamine). W. A. TURNER (*Amer. J. Sci.*, 1916, **41**, 339—343).—Two hundred c.c. of a metavanadate solution, containing about 0·16 gram of vanadium pentoxide and 1% of hydrochloric acid, are treated with 6% "cupferron" solution, the latter being added gradually until a slight excess is present, as is shown by the appearance of a white precipitate of nitrosophenylhydroxylamine. The precipitate is then collected on a filter, washed with a solution containing 6 c.c. of concentrated sulphuric acid and 1·5 grams of "cupferron" per litre, dried, ignited in a platinum crucible, and weighed as vanadium pentoxide. At the commencement of the ignition, a very small flame should be used, so that the vanadium pentoxide does not fuse before all carbon, etc., has been oxidised; the heat is then increased and the fused oxide caused to flow round the sides of the crucible in order to ensure complete oxidation. The method yields trustworthy results. The reaction between "cupferron" and a soluble vanadate in slightly acid solution is very sensitive, a red coloration being obtained with a solution containing 0·004 mg. of vanadium per c.c.; a precipitate is given by stronger solutions. W. P. S.

New Method for the Iodometric Estimation of Vanadium. Behaviour of Quinquevalent and Quadrivalent Vanadium towards the Halogen Acids. HUGO DITZ and FRIEDRICH BARDACH (*Zeitsch. anorg. Chem.*, 1915, **93**, 97—136).—The apparatus employed is that used for the estimation of chlorate by means of potassium bromide and hydrochloric acid (A., 1901, ii, 687). Pure ammonium metavanadate is used for the control experiments. At the ordinary temperature, quinquevalent vanadium is only very slowly reduced to the quadrivalent state by hydrochloric acid, but it is completely and rapidly reduced by potassium bromide and hydrochloric acid under suitable conditions, and the reduction does not proceed any further. A sufficiently large excess of acid must be present in order to shorten the time of the reaction. Potassium iodide and hydrochloric acid bring about reduction at the ordinary temperature to the tervalent stage, although a pure solution of quadrivalent vanadium is not further reduced under similar conditions.

The method is best carried out by placing 25 c.c. of the vanadium solution in the evolution apparatus, adding 10 c.c. of

a 10% solution of potassium bromide and 75 c.c. of concentrated hydrochloric acid, and allowing the reaction to proceed for five minutes. The small absorbing vessel contains a 5% solution of potassium iodide. When the reaction is over, 20 c.c. of 5% potassium iodide are added, the contents of the absorption vessel are washed back, and the solution is titrated with thiosulphate.

Sulphuric acid may be used in place of hydrochloric acid, but the latter is more convenient.

The principal reaction is: $V_2O_5 + 2KBr + 6HCl = 2VOCl_2 + Br_2 + 2KCl + 3H_2O$. C. H. D.

Analysis of Columbium–Tantalum Minerals, with Some New Tests for Columbium, Tantalum, and Titanium. JAMES MOIR (*J. Chem. Metall. Min. Soc. S. Africa*, 1916, **16**, 189—191).—The finely-divided mineral is fused with potassium hydroxide, the fused mass dissolved in twenty times its weight of water, and the solution filtered, the insoluble portion being washed with warm, dilute potassium hydroxide solution. The titanium remains insoluble as K_2TiO_3, along with iron and aluminium hydroxides, etc. The alkaline filtrate is treated with concentrated sodium hydroxide solution, when sodium tantalate crystallises in needles within a few minutes; if the liquid is now decanted, sodium columbate will separate out after several hours. Sodium columbate, when treated with ammonium oxalate, an acid, and zinc, gives a deep brown coloration, which changes to yellow as the reduction proceeds; the coloration is not changed by the addition of hydrogen peroxide. Titanium solutions treated in a similar way give a yellow coloration, which changes to orange-red with hydrogen peroxide. When potassium hyposulphite is added to an acid solution of columbic acid, a yellow precipitate forms; titanium solutions yield an orange-red coloration with this reagent. Columbic acid gives an orange precipitate with pyrogallol provided the solution does not contain an excess of mineral acid; tantalum gives a pale yellow precipitate. Concentrated sulphuric acid solutions of columbium yield characteristic colour reactions with certain phenols, but only yellow colorations are obtained in the case of tantalum. The reaction of titanium described by Lenher and Crawford (A., 1913, ii, 250) is rendered more sensitive by the addition of thiocyanate after reducing with zinc and hydrochloric acid. W. P. S.

Analysis of Commercial Benzols. P. E. SPIELMANN and E. G. WHEELER (*J. Soc. Chem. Ind.*, 1916, **35**, 396—399).—Toluene is estimated by distilling 100 c.c. of the benzol from an Engler flask at the rate of 7 c.c. a minute, and the volume of the distillate passing over up to 90° indicates by reference to a curve the quantity of toluene present in the mixture to an accuracy of about 1%. Carbon disulphide is estimated by determining the difference in specific gravity before and after its removal, as xanthate, by means of alcoholic potassium hydroxide and reference to a curve. After the removal of the carbon disulphide, the mixture consists essen-

tially of benzene, toluene, and paraffin; the toluene content being known, the specific gravity of such a mixture of benzene and toluene is found from the table, and the difference between this and the observed specific gravity is a measure of the paraffin content, the gravity of the paraffin in benzol being taken on the average as 0·730. The paper is illustrated by curves, diagrams, and numerous examples. G. F. M.

Solubility of Naphthalene in Ammonia. J. BRONN (*Zeitsch. angew. Chem.*, 1916, **29**, i, 172).—A reply to Hilpert (this vol., ii, 201). Whilst naphthalene is but sparingly soluble in liquid ammonia at its boiling point ($-38°$), at higher temperatures very considerable quantities are dissolved, and are re-deposited on cooling. G. F. M.

Ethereal Oils. Estimation of Eucalyptus Oil. SCHIMMEL & Co. (*Chem. Zentr.*, 1916, i, 55—56; from *Geschäftsber*, October, 1915).—The arsenic acid method is unsuitable in presence of alcoholic constituents, whilst the resorcinol method always gives good results.

The following constants are given for oil of milfoil: D^{15} 0·9339, $n_D^{20}=1{\cdot}47632$, acid number 5·6, ester number 24·3, acetyl number 86·8.

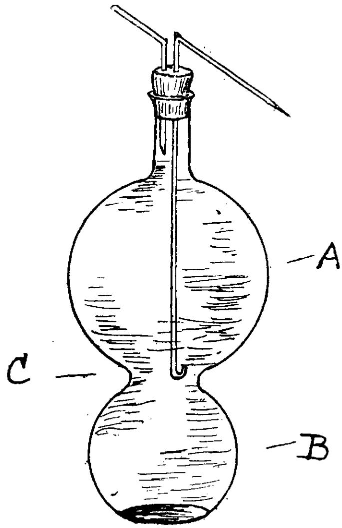
The statement of Sacher that the purity of vanillin can be estimated to 0·1% by titrating with $N/10$-potassium hydroxide was not confirmed. N. H. J. M.

Estimation of Alcohol in the Presence of Phenol. J. EHRLICH (*J. Ind. Eng. Chem.*, 1916, **8**, 240—241).—For mixtures containing from 8% to 20% of alcohol and 1% to 10% of phenol 50 c.c. of the sample are diluted with 30 c.c. of water, rendered strongly alkaline with concentrated sodium hydroxide solution, and distilled; 50 c.c. of distillate are collected. Twenty-five c.c. of the distillate are diluted with 30 c.c. of water, a slight excess of bromine is added, the excess is destroyed by the addition of a few drops of thiosulphate solution, an excess of sodium hydroxide is then added, the mixture distilled, and the alcohol estimated in the distillate by determining the specific gravity. The two distillations are necessary since small quantities of phenol pass over in the first distillation in spite of the excess of alkali in the solution. For higher concentrations of alcohol than those mentioned, 100 c.c. of distillate should be collected. W. P. S.

Content of Cholesterol and Fatty Substances in the Blood, together with a Modification of the Colorimetric Method for Estimating Cholesterol. FRANK A. CSONKA (*J. Biol. Chem.*, 1916, **24**, 431—438).—The amount of cholesterol in the blood in cases of pernicious anæmia is considerably below that found in the normal individual; the iodine number of the fatty acids of the anæmic blood varies from 53 to 103 (compare Medak, A., 1914, i, 355).

For the estimation of cholesterol, 2 c.c. of blood are measured

by an Ostwald pipette into a flask of the shape illustrated in the accompanying figure, and boiled with 20 c.c. of alcohol (95%), 4 grams of potassium hydroxide, and 2 c.c. of a 10% solution of barium chloride for one hour under a reflux condenser. After cooling, water is added up to the constriction and the cholesterol extracted by successive quantities of ether. After each extraction, the ethereal layer is brought to the constriction by adding a little water and is then blown by pressure into a separating funnel. The combined extracts are washed with water, the ether distilled off, and the cholesterol estimated by the intensity of the colour produced on treatment with acetic anhydride and concentrated sulphuric acid, as in the Autenrieth and Funk method. The addition of barium chloride to the saponification mixture eliminates almost entirely the yellow colour otherwise obtained in the final liquid. H. W. B.



A. *Upper bulb, about* 130 *c.c.*
B. *Lower bulb,* 70 *c.c.*
C. *Constriction,* 25 *mm. diameter.*

Estimation of Sucrose in Condensed Milk. G. W. KNIGHT and G. FORMANEK (*J. Ind. Eng. Chem.*, 1916, **8**, 28—31).—Sampling, clarification, and method of inversion are the principal features of the method proposed. The tin of condensed milk (after the removal of the label) is heated for a short time at 100°, cooled in a desiccator, weighed, and its contents then rinsed with hot water into a 500 c.c. flask; the tin is now dried and re-weighed. The contents of the flask are shaken to ensure solution of all sugar crystals, cooled, and diluted to 500 c.c. Two portions of 50 c.c. and 100 c.c., respectively, of the solution are transferred to separate 200 c.c. flasks, and each is treated successively with 1·7 c.c. of 5% phosphotungstic acid solution and 2·1 c.c. of normal lead acetate solution for each 10 grams of condensed milk in the respective portions. The mixtures are diluted to the mark, filtered, and portions of about 100 c.c. of the filtrates are treated with solid potassium oxalate, added in small quantities at a time, until the precipitate settles quickly, leaving a clear liquid; about 0·5 gram of the oxalate is usually sufficient, and an excess should be avoided. The mixtures are again filtered, and the filtrates polarised at 20°. The direct polarisation reading (P), corrected for the volume of the precipitate, is found by multiplying the reading of the weaker solution by 4 and subtracting the reading of the stronger solution

from the result. Two portions of 50 c.c. of the respective filtrates are now placed in 100 c.c. flasks, 5 c.c. of 38·8% hydrochloric acid are added to each, and the mixtures set aside at 20—25° for eighteen hours; they are then neutralised, diluted to 100 c.c., and polarised at 20°. The reading of the stronger solution is subtracted from 4 times the reading of the weaker solution, and the result multinlied by 2 to obtain the corrected invert polarisation (P'). The percentage quantity of sucrose (S) in the milk is then calculated from the equation $S = 26000(P - P')/W(141{\cdot}7 - t/2)$, where W is the weight of the sample and t the temperature of the polarisations. W. P. S.

Inversion of Sucrose by Invertase. Use of Salicylated Yeast. H. PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1915, **33**, 89—93. Compare this vol., ii, 157).—To ensure complete inversion of sucrose in such substances as molasses by means of yeast, it is necessary to take many circumstances into consideration. Molasses contain substances which retard the inversion, clarifying agents have the same effect, and even when the activity of the yeast is checked by a control inversion using pure sucrose under the same conditions, the rate of inversion is not the same in both cases. It always proceeds more slowly in the case of molasses than with pure sucrose. W. P. S.

Preparation of Invertase for the Estimation of Sucrose. W. A. DAVIS (*Bull. Assoc. Chim. Sucr. Dist.*, 1915, **33**, 94—97).—It is pointed out that pure invertase was used for the inversion of sucrose prior to the process described by Hudson (A., 1914, ii, 1147; compare T., 1886, **73**, 927); and that purification by treatment with lead acetate and dialysis is unnecessary, since autolysed yeast in the presence of toluene is stable for a long time. W. P. S.

Estimation of Pectin in Spices. TH. VON FELLENBERG (*Chem. Zentr.*, 1916, i, 530—531; from *Mitt. Lebensmittelunters. Hyg.*, **7**, 42—61).—The method depends on the estimation of the methyl alcohol in the pectin (compare A., 1915, i, 774). From 1 to 2 grams of the sample are placed on a filter and treated with small quantities of boiling 95% alcohol until the filtrate measures about 40 c.c.; after a similar treatment with light petroleum, the contents of the filter are dried, transferred to a flask, and distilled with 40 c.c. of water, 20 c.c. of distillate being collected. The mixture in the flask is now treated, while hot, with 5 c.c. of 10% sodium hydroxide solution, and, after five minutes, 2·5 c.c. of dilute sulphuric acid (1:4) are added, and 16·2 c.c. are distilled over; this distillate is mixed with 5 drops of sodium hydroxide solution and 5 drops of 10% silver nitrate solution and again distilled, 10 c.c. of distillate being collected and once more distilled. The final distillate, measuring exactly 6 c.c., is weighed. Three c.c. of it are then treated with 1 c.c. of an alcohol-sulphuric acid solution (21 c.c. of 95% alcohol and 40 c.c. of concentrated

sulphuric acid diluted with water to 200 c.c.) and 1 c.c. of 5% potassium permanganate solution. Comparison solutions containing 5 mg., 1 mg., and 0·3 mg. of methyl alcohol, respectively, are similarly treated at the same time. After two minutes, the mixtures are each treated with 1 c.c. of 8% oxalic acid solution, 1 c.c. of concentrated sulphuric acid, and 5 c.c. of magenta-sulphurous acid solution, and the colorations obtained are compared after the lapse of one hour. The pectin content of the sample is ten times that of the methyl alcohol. W. P. S.

Estimation of β-Hydroxybutyric Acid. P. A. SHAFFER and R. S. HUBBARD (*Proc. Amer. Soc. Biol. Chem.*, 1915, xxvii.; *J. Biol. Chem.*, 1916, **24**. Compare Shaffer and Marriott, A., 1914, ii, 77).—By increasing the strength of the sulphuric acid required in the oxidation of the β-hydroxybutyric acid to 10*N*, the oxidation is completed in twenty minutes, and the time required by the method of estimation thereby greatly shortened. H. W. B.

Detection and Estimation of Citric Acid in Wine. F. SCHAFFER and E. GURY (*Chem. Zentr.*, 1916, i, 389—390; from *Mitt. Lebersmittelunters. Hyg.*, 1915, **6**, 247—251).—A modification of Denigès's method is described, the quantity of citric acid being found from the volume of precipitate obtained. Twenty-five c.c. of the wine are rendered slightly alkaline with ammonia, evaporated to 10 c.c., then treated with 10 c.c. of 7% copper sulphate solution, and the mixture is evaporated to 10 c.c., cooled, diluted to 25 c.c., filtered, and 10 c.c. of the filtrate are heated with the addition of 1·5 c.c. of Denigès's reagent (compare A., 1915, ii, 847). After cooling, the mixture is filtered, the precipitate washed, and 1% potassium permanganate is added to the boiling filtrate until a brown coloration is obtained. A small quantity of hydrogen peroxide is added to destroy the coloration, and the mixture is submitted to centrifugal action in a graduated tube. The volume of the precipitate in c.c. multiplied by 0·021 gives the quantity of citric acid in grams per litre of wine. W. P. S.

Detection of Picric Acid in Urine and Viscera. E. KOHN-ABREST (*Ann. Falsif.*, 1916, **9**, 63—68).—Twenty c.c. of the urine are treated with 20 c.c. of mercuric sulphate solution (mercuric oxide, 20 grams, sulphuric acid, 40 c.c., and water, 200 c.c.), the mixture is filtered, and the filtrate is extracted with chloroform. The chloroform solution is mixed with 0·5 c.c. of water, the chloroform evaporated, and the residual aqueous solution is tested for picric acid. For this purpose, the picric acid is dyed on to wool or silk and the latter then treated with an alkaline potassium cyanide solution (*iso*purpurate reaction). The method will detect the presence of 0·005 gram of picric acid per litre of urine. In the case of viscera, the substance is extracted with 90% alcohol containing 1% of tartaric acid, the alcoholic extract is evaporated under reduced pressure, the residue obtained again extracted with alcohol, and the residue left on evaporating this extract is finally

treated with absolute alcohol. The alcoholic solution is filtered, the filtrate diluted with a small quantity of water, and evaporated under reduced pressure. The residual aqueous liquid is acidified with sulphuric acid (the acidity should be about 2%), extracted with ether, the ethereal solution evaporated, the residue dissolved in a small quantity of 1% tartaric acid solution, and extracted successively with light petroleum and ether. After these solvents have been separated, the aqueous solution is acidified with sulphuric acid, and the picric acid is extracted with ether. The picric acid may then be identified by the usual reactions. W. P. S.

Diazo-reaction for the Detection of Picramic Acid in Urine. HENRI PECKER (*J. Pharm. Chim.*, 1916, [vii], **13**, 268—269).—Ten c.c. of the urine are treated with 2 drops of 1% potassium nitrite solution and 5 drops of sulphuric acid (1:1) and then rendered slightly alkaline by the addition of β-naphthol dissolved in ammonia (D 0·925). A reddish-violet coloration is obtained if the urine contains picramic acid. The colour is soluble in ether. Urinary and biliary pigments do not interfere with the reaction. W. P. S.

Estimation of Salicylic Acid in Jams, etc. E. MÜLLER-HOESSLY (*Chem. Zentr.*, 1916, i, 388—389; from *Mitt. Lebensmittelunters. Hyg.*, 1915, **6**, 251—253).—Methods described by Heintz and Limprich (A., 1913, ii, 737) and by Serger are found to be suitable for the rapid estimation of salicylic acid, but more trustworthy are those proposed by von Fellenberg (A., 1910, ii, 906) and Philippe (A., 1912, ii. 932). In the latter method, the use of nickel basins is recommended, and the water-cooling apparatus is replaced by an air condenser. Fellenberg has mentioned that the result obtained should be increased by 10%, owing to the fact that this amount of salicylic acid is retained by the precipitate formed when the sample is clarified with lead acetate, and it is pointed out that this correction is also necessary in the estimation of salicylic acid by Philippe's method. W. P. S.

Rapid Method for the Estimation of Fat in Powders. S. B. PHILLIPS (*Analyst*, 1916, **41**, 122—123).—A quantity of the substance, containing from 1·5 to 3·5 grams of fat, is shaken in a wide-mouthed, stoppered bottle with 100 c.c. of trichloroethylene; after fifteen minutes, the stopper of the flask is replaced by a rubber stopper through which pass the stem of a 20 c.c. pipette and a short glass tube. The end of the pipette is provided with a filter consisting of two filter papers folded so as to form a thimble, which is tied on to a small, perforated cork, the latter being then fixed on to the pipette. When air pressure is applied through the short glass tube, the liquid is forced through the filter into the pipette, and the 20 c.c. of liquid thus collected are transferred to a weighed flask, the solvent is evaporated, and the residue of fat weighed. Owing to the increase in volume of the solvent, due to the dissolved fat, a correction has to be applied in calculating

the quantity of fat in 100 c.c. of the solvent. For instance, in the estimation of fat in cocoa, if the weight of fat in the 20 c.c. of solvent is 0·3 gram, this is multiplied by 5·040 to obtain the quantity in 100 c.c.; if the weight of fat is 0·70 gram, the factor 5·165 is used. W. P. S.

Determination of the Melting Point of Fats and Waxes. L. GOLODETZ (*Chem. Zeit.*, 1916, **40**, 223).—Small glass tubes about 3 cm. long sealed at one end are selected to fit fairly tightly over the bulb and lower portion of the stem of a thermometer. These are filled with about 0·2 gram of the fat, and the thermometer is pushed in as far as the bottom of the tube, so that a uniform layer of material is formed round the bulb. The fat is then melted by warming over a flame, and the whole is quickly placed in a glass tube to protect the thermometer from draughts and to ensure slow and regular cooling. The temperature at which the transparent layer of fat becomes cloudy is taken as the melting point. It is not identical with the solidifying point, as usually observed, but corresponds exactly with the true melting point. G. F. M.

The Estimation of Mixtures of Paracetaldehyde and Acetal. KENNEDY JOSEPH PREVITÉ ORTON and PHYLLIS VIOLET McKIE (T., 1916, **109**, 184—186).—Although acetal is hydrolysed very slowly in neutral or alkaline aqueous solution, hydrolysis occurs rapidly in the presence of hydrion. Thus a 1% solution of acetal in an $N/6000$-solution of a strong acid undergoes complete hydrolysis when boiled for a few minutes, whilst paracetaldehyde gives no trace of acetaldehyde in the distillate under such conditions.

For the estimation of acetal in the presence of paracetaldehyde it is therefore suggested that 0·2—0·4 gram of the mixture should be distilled with 30 c.c. of dilute acid containing hydrion at approximately $N/5000$-concentration; such a dilute acid solution is conveniently obtained by diluting 7 c.c. of $N/100$-acetic acid to 30 c.c. The distillate is collected in a little water or alcohol in a well-cooled receiver. For determining paracetaldehyde or the total acetal and paracetaldehyde, 30 c.c. of $N/5$-hydrochloric acid are used. Only a relatively small quantity of distillate need be produced, about 7 c.c. in the estimation of acetal and 10 c.c. in the case of paracetaldehyde. The acetaldehyde in the distillate is estimated by the method of Ripper (A., 1901, ii, 205) or of Seyewetz and Bardin (A., 1905, ii, 771), the latter being more rapid.

Typical results are quoted, and indicate the usefulness of the method. D. F. T.

Colorimetric Estimation of Cinnamaldehyde in Cinnamon. TH. VON FELLENBERG (*Chem. Zentr.*, 1916, i, 390—391; from *Mitt. Lebensmittelunters. Hyg.*, 1915, **6**, 254—266).—The value of cinnamon lies in its cinnamaldehyde content rather than in the quantity of total essential oil it contains. A method for the estimation of cinnamaldehyde depends on the coloration which de-

velops when the aldehyde is treated with sulphuric acid and *iso*butyl alcohol (compare A., 1911, ii, 667). One gram of the cinnamon is placed in a flask together with 40 c.c. of 95% alcohol, and the mixture is heated just to boiling for ten minutes, the flask being attached to a condenser, and any distillate collected in a 100 c.c. flask. From 30 to 35 c.c. of the alcohol are then distilled, 100 c.c. of boiled water are added to the flask, and the distillation is continued until the total distillate measures 100 c.c. Five c.c. of the distillate are then mixed with 2 c.c. of 5% *iso*butyl alcohol solution (in 95% alcohol) and 3 c.c. of 38% alcohol, 20 c.c. of concentrated sulphuric acid are added, and, after forty-five minutes, the coloration obtained is compared with that yielded by a known amount of cinnamaldehyde under similar conditions. The standard cinnamaldehyde solution used for comparison contains 2% of the aldehyde in 38% alcohol solution; it may be prepared from the aldehyde-sulphite compound and standardised by a bromine-iodine titration. Nine samples of Ceylon cinnamon were found to contain from 1·31 to 1·84% of cinnamaldehyde; seven samples of cassia-cinnamon contained from 1·23 to 2·77%, and a sample of cinnamon flowers 3·73%. W. P. S.

Colorimetric Estimation of Vanillin in Vanilla. TH. VON FELLENBERG (*Chem. Zentr.*, 1916, ii, 391—392; from *Mitt. Lebensmittelunters. Hyg.*, 1915, **6**, 267—274).—One gram of the finely-divided sample is boiled under a reflux apparatus with four successive quantities of about 20 c.c. of water, the extracts are diluted to 100 c.c., 0·5 gram of kieselguhr is added, and the mixture filtered. Fifty c.c. of the filtrate are extracted five times with alcohol-free ether, using 150 c.c. of the solvent altogether, the ethereal solution is treated with solid calcium chloride, filtered, evaporated to a small volume, and the remainder of the ether removed by a current of air. The residue is warmed to 60° with 30 c.c. of water, the solution filtered, and the filtrate diluted to 100 c.c. Five c.c. of this solution are then treated with 5 c.c. of 1% *iso*butyl alcohol solution (in 95% alcohol) and 20 c.c. of concentrated sulphuric acid, and the coloration produced is compared, after forty-five minutes, with that given by a known quantity of vanillin. It is recommended that the vanillin should be estimated separately in the outer and inner portions of the vanilla pod; in the case of normal vanilla, these two portions contain approximately the same quantity of vanillin, and a difference would indicate that some of the vanillin had been extracted from the outer portion. W. P. S.

Action of Titanous Chloride on Phenylhydrazine, Substituted Phenylhydrazines, and *p*-Nitrophenylhydrazones. F. ROBINSON (*J. Soc. Dyers*, 1916, **32**, 80—81; from *J. Manchester School Technol.*, **7**, 105).—Whilst phenylhydrazine and *p*-bromophenylhydrazine are unaffected by boiling with titanous chloride in acid solution, *p*-nitrophenylhydrazine is reduced quantitatively under these conditions to *p*-phenylenediamine and ammonia. The

reaction may be used for the volumetric estimation of *p*-nitrophenylhydrazine and acetone-*p*-nitrophenylhydrazone, excess of titanous chloride being employed, and subsequently titrated back with standard crystal-scarlet solution. An attempt to estimate acetone and formaldehyde volumetrically by precipitation of their nitrophenylhydrazones was not successful. G. F. M.

Indirect Method of Estimating Pyrimidine Groups in Nucleotides. WALTER JONES (*Proc. Amer. Soc. Biol. Chem.*, 1915, iii—x; *J. Biol. Chem.*, 1916, **24**).—The method is based on the discovery that in the acid hydrolysis of nucleic acids or nucleotides the phosphoric acid is liberated completely from the purine nucleotides in less than two hours, whereas its liberation from the pyrimidine nucleotides is a much slower, but regular, process. Hence the purine–phosphoric acid of a nucleotide-containing substance may be estimated by heating about 10 grams of it for two or more hours with 5% sulphuric acid and subtracting from the estimated free phosphoric acid the amount arising from the pyrimidine nucleotide, which has been found to be the equivalent of 10 mg. of magnesium ammonium phosphate per hour. The pyrimidine phosphoric acid is the difference between this value and the total phosphoric acid. H. W. B.

The Hydrochloride Method for the Estimation of Alkaloids. GEO. D. BEAL and ST. ELMO BRADY (*J. Ind. Eng. Chem.*, 1916, **8**, 48).—The method consists in extracting the alkaloid with ether, treating the ethereal solution with gaseous hydrogen chloride, evaporating the solvent, and weighing the residue of alkaloid hydrochloride. For the estimation of coniine in conium seeds, the powdered seeds are extracted with a mixture of ether, alcohol, and ammonia, the ethereal solution is separated, shaken with dilute sulphuric acid, and the acid aqueous solution, now containing the alkaloid, is rendered ammoniacal and extracted with ether. The ethereal solution is saturated with hydrogen chloride which has been dried by passing it through sulphuric acid, the solvent is evaporated, and the residue weighed. The residue is then dissolved in water, and the solution titrated with standard alkali solution, using phenolphthalein as indicator. The gravimetric and volumetric results thus obtained agree with each other and with those found by the method prescribed in the U.S. Pharmacopœia. The method may also be used for the estimation of alkaloids in colchicum root and tobacco. The alkaloid hydrochlorides in the three instances mentioned always separate from the ethereal solution partly in the form of crystals and partly as an oil. W. P. S.

Estimation of Small Quantities of Alkaloids. C. CARLINFANTI and M. SCELBA (*Boll. chim. farm.*, 1916, **55**, 225—232).—Part of this paper has been already published by E. Carlinfanti (A., 1915, ii, 709). Under the conditions given for the estimation of morphine, acetoxymorphine (heroine) may be estimated with considerable accuracy; it may be distinguished from morphine, since

it colours concentrated sulphuric acid containing nitric acid orange-yellow in the cold and blood-red in the hot, and does not reduce iodic acid. Codeine may also be estimated similarly, but for very small quantities of this alkaloid the method previously given (*loc. cit.*) is recommended.

*apo*Morphine may be estimated as follows: 1—5 c.c. of a 0·1% solution of the hydrochloride are evaporated to dryness in a basin on a water-bath. The residue is allowed to cool in a desiccator, and 10 c.c. of 95% alcohol and 0·1 gram of sodium hydrogen carbonate immediately added. The whole is then covered with a watch glass and mixed repeatedly during four to five hours, after which the liquid is poured into a tared flask and made up to volume with the washings of the residue with 95% alcohol. When the suspended sodium hydrogen carbonate has settled, a portion of the clear liquid is decanted into a colorimeter, and the emerald-green coloration which develops compared with that obtained from a known quantity of the alkaloid treated similarly. This method gives good results with quantities of *apo*morphine of the order 0·001—0·002 gram. For smaller amounts, the authors recommend the following modification of Grimbert and Leclère's method (A., 1915, ii, 192): To the solution of the alkaloid, made up with water to 3 c.c., are added 5 drops of saturated mercuric chloride solution and then 5 drops of 10% sodium acetate solution. The liquid is then boiled for half a minute, cooled, mixed with 1 c.c. of amyl alcohol, and introduced into a 50 or 100 c.c. flask, the vessel being washed out several times with small quantities of 95% ethyl alcohol, and the volume made up with concentrated alcohol. After being shaken, the liquid is left until the mercurous salt settles, the clear solution being compared in the colorimeter with one prepared similarly from a known weight of *apo*morphine.

In the case of strychnine, a definite volume of the solution containing at least 0·004—0·005 gram of the alkaloid is heated to boiling with 20—25 c.c. of 15% sulphuric acid solution, recently prepared bromine water being added drop by drop until the liquid assumes a pale yellow colour, and the boiling then continued for a few minutes; the presence of strychnine is revealed by a more or less intense reddish-violet coloration. Further addition of a few drops of bromine water turns the hot acid liquid pale yellow, and subsequent boiling renders it reddish-violet again. The cold solution is made up to 50 or 100 c.c., and its depth of colour matched with that of a solution prepared similarly from a known weight of the alkaloid. With a pharmaceutical preparation containing a strychnine salt, a quantity presumably containing at least 0·005 gram of the base is mixed with an alkali, and the mixture extracted with chloroform, the residue from the latter then being dissolved in 15% sulphuric acid solution and treated as above.

Under the conditions employed in the case of strychnine, brucine gives a salmon-red coloration with bromine water, but, when the alkaloid is present in small proportion, the second addition of bromine water renders the solution colourless. With strychnine, on the other hand, the violet-red coloration persists almost un-

altered after a second and even a third treatment with bromine water. In conformity with this behaviour, the proportion of strychnine in *Nux vomica* preparations and other solutions containing strychnine and brucine in approximately equal proportions may be estimated by means of bromine water in the manner described above. T. H. P.

Estimation of Caffeine in Tea by the Sublimation Method. E. PHILIPPE (*Chem. Zentr.*, 1915, ii, 1217—1218; 1916, i, 387—388, 529; from *Mitt. Lebensmittelunters. Hyg.*, 1915, **6**, 177—191, 233—247; **7**, 37—42. Compare A., 1912, ii, 932).—Further investigation of the sublimation method (compare A., 1914, ii, 285) shows that it yields trustworthy results, especially when the amount of sublimed caffeine does not exceed 100 mg. The caffeine is extracted completely from the ammoniacal tea by four successive treatments with chloroform. If the tea is not treated with ammonia before the extraction, the caffeine present in combination is not obtained in solution. The loss of caffeine brought about by extracting the acid solution of the caffeine with ether to remove certain impurities does not exceed 0·06%.

From 1·56% to 3·93% of caffeine was found in 39 samples of tea examined by the sublimation method; the author does not agree with Müller-Hoessly (this vol., ii, 353) that simple air-cooling can replace the cold-water condenser, and there is no advantage in using nickel basins in place of glass basins. The water content of the samples varied from 6·87% to 13·85%, and appeared to indicate to some extent the origin of the teas. The samples contained from 0·5% to 37% of stalks; as a rule, the presence of stalks diminished the caffeine content, but there was no strict relation between the quantities of caffeine and stalks in the samples.

Comparative estimations showed that the sublimation method yielded results which agreed with those found by Lendrich and Nottbohm's method (A., 1909, ii, 449); the results obtained by Keller's method were less trustworthy. In using Lendrich and Nottbohm's method for the estimation of caffeine in tea, the author operates on 5 grams of the powdered sample, treating this quantity with 10 c.c. of ammonia, and continuing the process as for the estimation of caffeine in coffee. In the case of tea, however, it is not necessary to add solid paraffin for the separation of fatty substances. W. P. S.

Estimation of Creatine in Muscle. II. LOUIS BAUMANN and HARRY M. HINES (*J. Biol. Chem.*, 1916, **24**, 439—442. Compare A., 1914, ii, 227).—The authors find that the estimation of creatine in muscle by Baumann's acid hydrolysis method (*loc. cit.*) affords results which agree closely with those obtained by Janney and Blatherwick's aqueous extraction method (A., 1915, ii, 711).

H. W. B.

Occurrence and Estimation of Creatine in the Urine. F. H. McCRUDDEN and C. S. SARGENT (*J. Biol. Chem.*, 1916, **24**, 423—429).—The authors find that Folin's newer method for the

estimation of creatine in the urine (A., 1914, ii, 505), which depends on the conversion of creatine into creatinine by boiling with picric acid, indicates the presence of creatine in normal urines which according to other methods really do not contain it. Since pure creatine is accurately estimated by the newer method, the authors infer that human urine contains a substance or substances other than creatine which give a colour reaction similar to that of creatinine on boiling with picric acid; this, therefore, may appear in the results as creatine. H. W. B.

Estimation of Nicotine in Tobacco and Tobacco Extracts. A Critical Examination of Methods. HANS BAGGESGAARD RASMUSSEN (*Zeitsch. anal. Chem.*, 1916, **55**, 81—131).—Precipitation of nicotine with silicotungstic acid (compare Bertrand and Javillier, A., 1909, ii, 450; 1911, ii, 827) having been found to yield trustworthy results, the author recommends the following procedure for the estimation of nicotine in tobacco and tobacco extract. Ten grams of the dry, powdered tobacco are mixed in a flask with 8 c.c. of a mixture consisting of three parts of 33% sodium hydroxide solution and one part of alcohol, 50 c.c. of ether and 50 c.c. of light petroleum are added, the flask is closed and its contents are shaken at intervals for five hours. The liquid is then filtered through a covered filter, 50 c.c. of the filtrate are shaken with 25 c.c. of 1% hydrochloric acid, the acid layer is separated and treated with about 10 c.c. of 12% silicotungstic acid solution. After ten hours the precipitate is collected, washed with 1% hydrochloric acid, dried at 120°, and weighed. The weight of the precipitate multiplied by 0·1012 gives the quantity of nicotine. In the case of tobacco extract, 4 grams of the substance are mixed with 5 c.c. of 33% sodium hydroxide solution and 5 c.c. of water, and 25 c.c. each of ether and light petroleum are added. The mixture is shaken for five hours, then filtered, and the nicotine precipitated as described. The precipitate may also be ignited together with the filter in a platinum crucible, and the residue weighed; the weight of this residue multiplied by 0·1140 gives the quantity of nicotine. The presence of ammonia does not interfere with the results obtained. Pyridine causes the results to be slightly too high, especially if it is present in considerable quantity. Distillation with steam from an acetic acid solution appears to be the best method of separating pyridine from nicotine; the pyridine is volatile, whilst the nicotine remains in the acid solution. Kissling's method (A., 1882, 1005) and Koenig's method (A., 1911, ii, 670, 1143) were found to be trustworthy; Keller's and Toth's methods (A., 1899, ii, 193; 1901, ii, 363, 708) yielded less accurate results, and Ulex's method (A., 1911, ii, 334) was untrustworthy. Degrazia's method yielded low results, owing to the fact that the whole of the nicotine does not distil under the conditions prescribed; Thoms's method (A., 1900, ii, 428) is tedious, and the nicotine is liable to be contaminated by other substances which are also precipitated by the potassium-bismuth iodide reagent.

W. P. S.

Colour Reactions for Indole and Scatole. V. E. NELSON (*J. Biol. Chem.*, 1916, **24**, 527—532).—If a few drops of dimethylaniline are thoroughly emulsified with 5 c.c. of scatole solution in a test-tube, and concentrated sulphuric acid is added cautiously down the side of the tube so as to form a layer at the bottom, a violet ring forms at the junction of the two liquids, which is still visible at a dilution of one part in a million. The substance producing the violet colour is soluble in chloroform. Indole produces a faint red colour in similar circumstances; the coloured substance, however, is insoluble in chloroform.

When a few crystals of methylglyoxal and a crystal of ferric sulphate are substituted for the dimethylaniline in the above test, a yellow colour soluble in amyl acetate is formed with scatole and a reddish-violet ring with indole solutions. Similarly, glycollic acid gives a deep reddish-violet colour with scatole and a brown colour with indole, whilst glyceraldehyde produces red and yellow colours respectively.

The following tests for scatole and indole involving the use of vanillin are sensitive to dilutions of from one part in two millions to one in five millions: A few drops of a 5% solution of vanillin in 95% alcohol are added to 5 c.c. or 6 c.c. of the indole solution, and the mixture is then made strongly acid with 3 c.c. or 4 c.c. of concentrated hydrochloric acid; a deep orange colour is produced. With scatole solution, a deep violet colour is formed on heating. Sulphuric, phosphoric, or hydrofluoric acid may be substituted for the hydrochloric acid without materially affecting the result. The violet colour formed from scatole, vanillin, and phosphoric or hydrofluoric acid changes to orange when shaken with chloroform, whereas the violet colour produced when hydrochloric or sulphuric acid is employed is stable, and dissolves as such in the chloroform. Since the colour produced by indole is only slightly soluble in chloroform, this test serves for the detection of scatole in the presence of indole. Tryptophan also gives a deep red to violet coloration with vanillin and sulphuric acid, but the coloured substance is insoluble in chloroform, and the reaction is not so sensitive as with indole and scatole.

Vanillin dissolved in amyl, butyl, or propyl alcohol gives characteristic colour reactions with hydrochloric, sulphuric, or phosphoric acid. Vanillin in acetone solution gives a deep blue coloration on the addition of hydrochloric acid. A rose-red colour is developed when xylene, vanillin, and hydrochloric acid are shaken together. H. W. B.

Improved Gas Chain Methods of Estimating Hydrogen Ion Concentration in Blood. J. F. MCCLENDON (*J. Biol. Chem.*, 1916, **24**, 519—526. Compare A., 1915, ii, 669).—The author details certain improvements in the apparatus already described (*loc. cit.*). H. W. B.

General and Physical Chemistry.

A Vacuum Spectrograph for High Frequency Spectra and a Preliminary Investigation of the Rare Earths. MANNE SIEGBAHN and EINAR FRIMAN (*Physikal. Zeitsch.*, 1916, **17**, 176—178).—The vacuum spectrograph described has been used in the examination of the high frequency spectra of the rare-earth elements, the finely powdered salts of which were rubbed on to the roughened surface of a copper disc serving as anticathode. The wave-length measurements of the α_1 and α_2 lines are recorded for the series beginning with praseodymium (atomic number 59) and ending with tantalum (atomic number 73). In this series there is a gap between neodymium (60) and samarium (62). The sequence of the rare-earth elements, indicated by the high frequency spectral measurements, is in complete agreement with that which is generally accepted on the basis of atomic weight determinations. H. M. D.

Spectrochemical Notices. K. VON AUWERS (*Ber.*, 1916, **49**, 827—834).—I. For making a series of readings, and especially for controlling measurements with the hydrogen lines, the author strongly recommends the use of the D_3 line of the helium spectrum instead of the sodium line. He has had a clamp made to hold a hydrogen and a helium tube so that the light from either can be used at will, and formulæ for converting indices obtained with the D_3 line into the sodium line indices have been calculated.

II. The measurement of refraction and dispersion is discussed, and some cases of exalted molecular dispersion are reviewed. It is shown that the values of $E\Sigma_\alpha$ and $E\Sigma_D$ are sufficient as a measure of the exaltation of the refractivity and $E\Sigma_\beta - E\Sigma_\alpha$ and $E\Sigma_\gamma - E\Sigma_\alpha$ as a measure of the exaltation of dispersion.

III. Harries (A., 1915, i, 966) attempted to obtain evidence as to the constitution of piperylene by examining its ozonide, but without success. He quoted optical constants, however, which are now shown to indicate conclusively the formula

$$CHMe{:}CH{\cdot}CH{:}CH_2,$$

which Thiele proposed. Harries's specimen must have been fairly pure. J. C. W.

The Breadth of Spectral Lines. WILLEM CORNELIS MANDERSLOOT (*Jahrb. Radioaktiv. Elektronik,* 1916, **13**, 1—55).—A theoretical paper in which the author discusses the factors which have an influence on the breadth of spectral lines, such as the Doppler effect, the damping due to radiation, and the effect of the rotation of the molecules.

The chief conclusions arrived at are that the ultra-red absorption spectra of gases are due to vibrations of charged atoms, and that the form of the absorption curve is largely influenced by molecular rotation. Whereas diatomic compound gases exhibit a double

absorption band, this is not shown by the elements which form diatomic molecules in the gaseous state. It follows from this that the component atoms of the molecules of the elements are not electrically charged. H. M. D.

The High Frequency Spectra of the Elements Arsenic–Rhodium. MANNE SIEGBAHN and EINAR FRIMAN (*Ann. Physik*, 1916, [iv], **49**, 611—615. Compare this vol., ii, 167, 205).—Wave-length measurements of the lines α_1, α_2, β_1, and β_2 (K series) in the spectra of arsenic, selenium, bromine, rubidium, strontium, columbium, and rhodium are recorded. For each series of lines the square root of the frequency is a linear function of the atomic number as required by Moseley's formula. The wave-lengths of the cæsium lines have also been measured. H. M. D.

The High Frequency Spectra (L-Series) of the Elements Tantalum to Bismuth. MANNE SIEGBAHN and EINAR FRIMAN (*Ann. Physik*, 1916, [iv], **49**, 616—624. Compare preceding abstract).—Previous measurements of the wave-lengths of lines in the spectra of these elements have been extended, with the result that the existence of at least eleven different groups of lines has been established. The wave-lengths of these are recorded, and it is shown that the Moseley relation between the frequency and the atomic number of the element holds for each group of lines.
H. M. D.

The Emission Spectrum of Diatomic Compound Gases in the Remote Ultra-red. W. MANDERSLOOT (*Ann. Physik*, 1916, [iv], **49**, 725—730).—A theoretical paper, in which it is shown that translational movement of diatomic compound molecules has no influence on the emission spectrum, which is due to the rotation of the molecules. A formula is derived, from which the position of the maximum on the distribution curve may be calculated, and a relation connecting the near and the remote regions of the infra-red emission spectrum is also given.

The elementary gases show no absorption in the infra-red, and from this it is inferred that the molecules of these gases are not electrically bipolar. H. M. D.

The Infra-red and Ultra-violet Absorption of Sulphur Dioxide and their Relation to the Infra-red Spectra of Oxygen and Hydrogen Sulphide. C. SCOTT GARRETT (*Phil. Mag.*, 1916, [vi], **31**, 505—511).—The wave-lengths of the centres of the bands in the ultra-violet absorption spectrum of sulphur dioxide have been determined, the absorption being measured photographically with the aid of a quartz spectrograph and a Hilger rotating sector photometer.

The region of absorption is divisible into three parts, characterised by constant differences between the wave-numbers of successive band-centres. Between λ 3182 and λ 2802 this difference is 22·4 for twenty successive bands; between λ 2324 and λ 2107 the

constant difference is 34·4 for fourteen bands, and in the intermediate region there are twenty-one bands with a difference of 12 in the successive wave-numbers.

The analysis of the experimental data in relation to Baly's theory (compare A., 1914, ii, 318; 1915, ii, 77, 714) of the connexion between ultra-violet and infra-red absorption has shown that the wave-number differences can be expressed in terms of four basis constants, 0·2, 2·8, 4, and 4·3. According to Coblentz's data, the wave-numbers of the infra-red absorption bands can be expressed as multiples of 9·632, which is the product of all four basis constants. Since the basis constants are characteristic of the sulphur and oxygen atoms in the compound, it was to be expected that these constants would be applicable to the absorption spectra of oxygen and hydrogen sulphide. Coblentz's data for these gases show, indeed, that the wave-numbers of the bands in the infra-red spectrum of hydrogen sulphide are multiples of 4·3, which constant is therefore characteristic of the sulphur atom, and that the wave-numbers of the bands in the infra-red spectrum of oxygen can be expressed in terms of the product of 2·8 and 4.

H. M. D.

The Ultra-violet Absorption System of Sulphur Dioxide. E. C. C. Baly and C. S. Garrett (*Phil. Mag.*, 1916, [vi], **31**, 512—520. Compare preceding abstract).—Accurate measurements of the wave-lengths of the component lines of the bands in the ultra-violet absorption spectrum of sulphur dioxide by Miss Lowater (*Astrophys. J.*, 1910, **31**, 311) have made it possible to deduce more accurate values for the wave-number constants, and to subject the theory of the relation between infra-red and ultra-violet absorption to a more rigid test than has been possible for the compounds which have been previously examined.

In the previous paper the wave-length of the centre of the less refrangible ultra-violet band was found to be λ 2961, corresponding with the wave-number 33780, but the more accurate data give 33751·6 as the central wave-number. From this are derived the three basis constants 2·73, 4·32, and 8·177, which yield by multiplication in pairs $2·73 \times 8·177 = 22·3225$, which is the constant difference of the wave-numbers for the less refrangible ultra-violet band, $4·32 \times 8·177 = 35·324$ the constant difference for the more refrangible band, and $2·73 \times 4·32 = 11·794$ the difference characteristic of the region between the two bands.

According to Baly's theory, the wave-numbers of the centres of the sub-groups in the less refrangible ultra-violet band are consequently given by $33751·6 \pm n \times 223·225$, where $n = 0, 1, 2, 3, \ldots$ The fundamental infra-red band with the wave-number 223·225 is, according to Bjerrum, of complex structure and consists of a group of lines, the wave-numbers of which are given by $223·225 \pm \nu_r$, where ν_r depends on the basis constants 2·73 and 8·177. Since $8·177 = 3 \times 2·73$ almost exactly, the structure of the fundamental band is given by $223·225 \pm n \times 2·73$, where $n = 0, 1, 2, 3, \ldots$ Taking into account the number of lines on opposite sides

of the central line and the number of sub-groups on each side of the central sub-group, it is found that the whole system of lines in the less refrangible ultra-violet band may be expressed by the formula $33751 \cdot 6 + p \times 223 \cdot 225 + n \times 2 \cdot 73$, where $p = -7, -6 \ldots, 0 \ldots, +12, +13$, and $n = -44, -43 \ldots, 0 \ldots, +36, +37$. The entire group of bands consists therefore of 21 sub-groups, each containing 82 absorption lines. This corresponds with the existence of 82 series, each containing 21 lines, with a constant difference between the wave-numbers equal to 223·225.

The wave-numbers of these lines have been calculated and compared with the observed values, the agreement being exceedingly good. The comparison is considered to afford further support for the theory that the infra-red and ultra-violet absorption spectra are related in a simple quantitative manner. H. M. D.

Relationship between the Physical Properties of Solutions. V. Ultra-violet Dispersion of Salts in Water. ADOLF HEYDWEILLER and OTTO GRUBE (*Ann. Physik*, 1916, [iv], **49**, 653—670. Compare A., 1913, ii, 645).—Measurements have been made of the refractive index of aqueous solutions of lithium sulphate, chlorate, acetate, thiocyanate, manganese chloride, nickel chloride, and lead acetate for ultra-violet light of different wave-lengths. The selection of lithium salts for this investigation is due to the fact that these salts are relatively transparent towards ultra-violet light, whilst the lithium ion has but little influence on the measured refraction and dispersion.

The tables show the values of $(n - n_0)$ and $\Delta_n = 100(n - n_0)/mn_0$, where n and n_0 are the refractive indices for the salt solution and water respectively, and m is the equivalent concentration of the solution. The data are found to be in satisfactory agreement with the equation $\Delta_n = B_n + (A_n - B_n)i$, in which i is the degree of ionisation of the salt and A_n and B_n are constants.

In a theoretical discussion of the results it is shown that the ultra-violet dispersion can be interpreted in terms of Drude's equation. This equation is made use of in calculating the frequency of vibration of the valency electrons of the sulphate, chlorate, chloride, acetate, and thiocyanate ions. The frequency in question is almost independent of the nature of the cation with which the anions are associated, although cations of the heavy metals exert a measurable influence. H. M. D.

The Colour of Polyhydroxyanthraquinone Dyes. DAVID B. MEEK and EDWIN ROY WATSON (T., 1916, **109**, 544—561. Compare this vol., ii, 2).—In an earlier paper it was suggested that the vibration causing the colour of a dye is a change, or tendency to change, from one quinonoid form to another, involving alternation of double and single linkings along a conjugate chain. In connexion with this theory it was shown that for dyes of similar structure the wave-lengths of the maxima of absorption were in the ratios of the numbers of double bonds in the chains. The effect of varying the nature, but not the lengths, of the conjugate

chains has now been investigated. The dyes chosen for examination were, to give them systematic names, 1:2-di-, 1:4-di-, 1:2:4-tri-, 1:2:3-tri-, 1:2:5:8-tetra-, 1:2:4:5:8-penta-, 1:2:4:5:6:8-hexa-, and 1:2:3:5:6:7-hexa-hydroxyanthraquinones. The changes have been made by (1) altering the end groups, which was studied by observing the absorption spectra of each dye separately in alcohol, in potassium hydroxide, and on tin, alum, and chrome-mordanted wool, and by (2) varying the numbers and positions of the auxochromes, which was investigated by comparing the different dyes under the same conditions.

In section (1) it was observed that, except in the case of purpurin, the maxima of the absorption bands are shifted towards the red end of the spectrum on passing from the free dye to its salts, and that the amount of displacement rises with the positivity of the metallic radicle. If it is assumed that the conjugate chain is in a state of tension, its oscillation will be shorter the greater the tension, and this tension will be greater the more firmly the metallic radicle is attached to the dye, that is, the more positive this radicle is. This interpretation of the results is discussed in connexion with Hantzsch's theories on the colours of violurates (A., 1910, i, 200) and with Baly's views.

No simple generalisations under section (2) could be made, but the results lead the authors to criticise the conclusions which Georgievics came to on the influence of the hydroxyl groups on the colours of the "lakes" of these dyes (A., 1911, i, 546). The following suggestions are nearer the truth: (*a*) two hydroxyl groups in one benzene nucleus, ortho or para to one another, are necessary to the production of a "deep" colour (red, violet, or blue); (*b*) if both benzene nuclei contain such pairs of hydroxyl groups the colour is still deeper; (*c*) three hydroxyl groups in the 1:2:4-positions in one benzene nucleus produce a deeper colour than a pair in the ortho- or para-position; (*d*) three hydroxyl groups in the 1:2:3-positions in one nucleus produce a brown colour.

It appears that absorption spectra of dyes on the fabric had not been studied before, and the necessary manipulation is described. J. C. W.

The Absorption of Gas by Quartz Vacuum Tubes. R. S. Willows and H. Trevelyan George (*Proc. Physical Soc. London*, 1916, **28**, 124—131).—A new quartz tube, through which an electrodeless discharge is passed, does not absorb air. If the tube is previously filled with hydrogen, which is absorbed by the quartz when the discharge passes, it is found to have acquired the power of absorbing air under the influence of the current. If discharges in hydrogen are alternated with those in air, the bulb can be made to absorb large quantities of either gas, and the activity towards both air and hydrogen gradually increases.

In explanation of the observations, it is suggested that oxidation products are formed when the discharge is passed through air, and that these products are reduced by hydrogen. The

alternating processes are compared with those which occur in a storage battery, the absorption of hydrogen corresponding with the charging and that of air with the discharging of the cell. In support of the theory, it has been found that the readiness with which hydrogen is absorbed diminishes when the quartz tube is subjected to the action of reducing agents after the air treatment.

H. M. D.

The Electric Spark as a Pulveriser of Solutions, and its Use in order to obtain a Monochromatic Light. GUILLAUME HIRSCHEL (*Rec. trav. chim.*, 1916, **36**, 110—115).—The apparatus used is a modification of the spark-producer of Delachanal and Marmet (*Ann. chim. phys.*, 1841, [iii], **3**). To the tube are sealed two side-tubes, one at the level of the spark and the other at the top of the tube, to serve respectively as inlet and outlet for the particular gas or air used. The bottom platinum wire, acting as cathode, is surrounded by a stout capillary tube 0·5 mm. wider than the wire, and extending above it by 1 mm. The capillary is slightly opened at the base to permit the solution easily to reach the electrode. The apparatus can be so arranged in size, if necessary, that one drop of solution is sufficient to fill the capillary and be pulverised. To produce a coloured flame with the salt, hydrogen, by preference, is passed through the apparatus and burnt as it issues, arranging the flow of gas to get a flame 1 cm. high. If ordinary coal-gas is to furnish the flame, air is passed through the apparatus and into the air-holes of a Bunsen burner. A sketch of the arrangement is shown by which this apparatus can be used in conjunction with a Laurent lamp to furnish an excellent sodium light for polarimetric work, the intensity being nearly twice as great as that of the ordinary lamp. The pulveriser uses 2 amperes at 30 volts and can be worked with an alternating current, using Caldwell's contact-breaker. W. G.

Electron Theory of the Metals. A. MARCH (*Ann. Physik*, 1916, [iv], **49**, 710—724).—By the application of the theory of quanta, a formula is obtained which connects the number of free electrons with the free periods of vibration of the atoms of the different metals. When these free periods are changed by compression of the metal or by the formation of an alloy, there is a corresponding alteration in the number of free electrons, which shows itself in a change in the electrical conductivity. Attention is drawn to the relation between the conductivity and the hardness of alloys formed by gold and silver and by gold and copper. In both these isomorphous mixtures the maximum of hardness corresponds with a minimum on the conductivity curve. The existence of this relation affords some evidence in support of the author's theoretical deductions. H. M. D.

Measurements of Conductivity in Soap Films. WALTER RICKENBACHER (*Koll. Chem. Beihefte*, 1916, **8**, 139—170).—The

electrical conductivity of a number of soap films has been examined in reference to the influence of the concentration of the soap and to the effect produced by the addition of glycerol and potassium nitrate.

In coloured soap films the conductivity increases as the thickness approaches its lower limit. The increase is less marked in more concentrated solutions. It is attributed to the accumulation of the dissolved substances in the surface layers.

When the thickness of the films is reduced to that corresponding with the dark spot, the above-mentioned effect is no longer observed. The discontinuity at the boundary separating the dark and the coloured layers is supposed to be due to differences in the concentration of the dissolved substances. The electrical measurements give 12 $\mu\mu$ as the lower limit of thickness of the first dark film, but evidence of a second order of dark film has been obtained corresponding with a thickness of 7·3 $\mu\mu$. H. M. D.

Influence of Temperature on the Electrical Conductivity of Certain Feeble Acids. E. OLIVERI-MANDALÀ (*Gazzetta*, 1916, **46**, i, 298—323).—The observations of various investigators having indicated that increase of the ionisation constant with rise of temperature is a characteristic of weak electrolytes, the author has extended such measurements to amides, hydroxamic acids, etc., for which desmotropic forms are possible in solution, and to tetrazole and 1 : 2 : 3-triazole derivatives, which have free either a carboxyl group or an iminic hydrogen atom or both. The compounds examined were: azoimide, benzhydroxamic acid, benzamide, 4-phenyl-1 : 2 : 3-triazole, 4-cyano-5-methyl-1 : 2 : 3-triazole, γ-methyl-*iso*oxazolone, 2-methyltetrazole-5-carboxylic acid, 2-methyl-1 : 2 : 3-triazole-4-carboxylic acid, 5-phenyl-1 : 2 : 3-triazole-4-carboxylic acid, and 5-methyl-2-ethyl-1 : 2 : 3-triazole-4-carboxylic acid.

The results obtained show that the carboxylic acids derived from tetrazole and triazole exhibit behaviour analogous to that of aliphatic and aromatic carboxylic acids, rise of temperature being accompanied by gradual diminution of the degree of ionisation and the electrolytic dissociation constant; the absolute temperature-coefficients of the conductivity also decrease as the temperature rises, and the percentage-coefficients vary between 1 and 2 in the region of temperature, 0—40°. The opposite behaviour is shown by tetrazole and triazole derivatives containing, not a free carboxyl group, but an iminic hydrogen, and also by benzamide and azoimide; for these compounds the percentage temperature-coefficients of the conductivity are high, and the degree of dissociation and the magnitudes derived from it increase as the temperature rises.

For 2-methyltetrazole-5-carboxylic and 2-methyl-1 : 2 : 3-triazole-4-carboxylic acids, which contain the same substituents, the values of K are respectively 0·00052 and 0·0142. This difference is due to the diverse influences of the two nitrogenated nuclei on the carboxyl group. Tetrazole and triazole have the respective constants $1·4 \times 10^{-5}$ and $1·6 \times 10^{-12}$, and should, therefore, act as substituents having widely different effects on the value of K.

Comparison of the results with those given by other investigators shows that not only feebly dissociated compounds have high percentage temperature-coefficients of conductivity. Thus, the latter is the case with bistetrazole, tetrazolamide, and nitrourethane, although their dissociation constants are of the same order of magnitude as those of the stronger organic acids. It is not justifiable to assume the existence of tautomeric phenomena to explain such abnormal behaviour, since it would not be valid in the cases of azoimide, aniline, lævulose, sucrose, acetoxime, etc., which have high temperature-coefficients, although intramolecular change in solution is excluded.

The heats of ionisation of the electrolytes considered have been calculated by means of van't Hoff's equation, $d \log K/dT = -q/RT^2$. A high positive heat of ionisation is shown by azoimide, benzamide, tetrazole and its derivatives, and triazole, that is, in general by electrolytes containing an iminic hydrogen. The other compounds, containing carboxyl, behave like carboxylic acids of the aliphatic and aromatic series, their heats of ionisation being negative and very small; benzhydroxamic acid forms an exception, since it behaves like a true oxygenated organic acid.

With most of the above electrolytes which exhibit very high heats of ionisation, different desmotropic forms may exist in solution, so that it is questionable whether the calculated heat of ionisation includes the thermal effect of such chemical transformation. With other compounds, among them water, such explanation of a high heat of ionisation is not, however, possible. The conclusion is drawn that at present no relation can be established between the heat of ionisation of an electrolyte and its chemical constitution.

T. H. P.

A New Method of Determining Ionic Velocities. CONSTANCE HARRISON GRIFFITHS (*Proc. Physical Soc. London*, 1916, **28**, 132—147).—The method consists in determining the change in weight of the cathode and the electrolyte in its neighbourhood by suspending the cathode and the cylindrical tube in which this is mounted from the beam of a balance. The tube is open at the lower end, and in the experiments described, which were made with copper sulphate solution, the cathode consisted of a perforated copper disc. In calculating the ionic mobilities from the rate of change of weight of the suspended system during the passage of a current, corrections are applied for the change in volume of the cathode and for the change in the density of the surrounding solution. H. M. D.

An Explanation of the Migration of the Ions. S. W. J. SMITH (*Proc. Physical Soc. London*, 1916, **28**, 148—156).—The usual graphic method employed to illustrate the changes in concentration which occur on the passage of a current through a solution is considered to be imperfect, and an attempt is made to give a more precise account of the mechanism of electrolysis. H. M. D.

A Method of Exhibiting the Velocity of Iodine Ions in Solution. S. W. J. SMITH (*Proc. Physical Soc. London*, 1916, **28**, 157—161).—Since dilute solutions of potassium chloride and potassium iodide of the same molar concentration have very nearly the same electrical conductivity and the potential difference at the surface of contact is negligibly small, the combination of these solutions affords a convenient means for measuring the mobility of iodine (or chlorine) ions. The line of separation of the two solutions, which are contained in a U-tube, is made clear by the addition of a small quantity of mercuric chloride to the two solutions. The moving boundary consists of a thin, yellow disk of mercuric iodide, which is not appreciably soluble in the potassium chloride solution.

If the current is first passed in the direction which causes the iodine ions to travel towards the chloride solution, the chlorine liberated at the anode affords a means of redetermining the velocity of the ions when they are caused to move in the opposite direction by reversal of the current. H. M. D.

Potential Relations of Aluminium and Zinc. CH. M. VAN DEVENTER (*Chem. Weekblad*, 1916, **13**, 475—478).—In dilute sulphuric or nitric acid aluminium is electropositive to zinc, but amalgamated aluminium is electronegative to this metal.

A. J. W.

Galvanic Exaltation of Metals in Aqueous Solution. CH. M. VAN DEVENTER (*Chem. Weekblad*, 1916, **13**, 472—475).—A lead rod coated with lead sulphate, and immersed in an aqueous solution of sulphuric acid, is electropositive to a lead rod without the coating. A. J. W.

The Free Energy of Hydrochloric Acid in Aqueous Solution. JAMES H. ELLIS (*J. Amer. Chem. Soc.*, 1916, **38**, 737—762).—The best practical definition of ion activity or "effective ion concentration" is afforded by the equation $F_1 - F_2 = RT \log (a_1/a_2)$, in which $F_1 - F_2$ represents the decrease in the free energy of the system attending the transfer at the absolute temperature T of 1 mol. of any substance, for example, an ion, from a solution of any concentration in which its activity is a_1, to another in which its activity is a_2. The free-energy decrease, $-\Delta F$, is best determined by measuring the *E.M.F.* of cells in which such a transfer takes place. This investigation deals with the measurement of the *E.M.F.* of cells of the type H_2 (gas) | HCl (at concentration c) | Hg_2Cl_2 (solid) + Hg. From the difference between the observed *E.M.F.* of two such cells in which the acid concentrations are c_1 and c_2 the free-energy difference can be calculated, and hence by the above equation the activity ratio can be determined.

By taking every possible precaution, calomel electrodes have been prepared which are reproducible to 0·05 millivolt when in contact with hydrochloric acid of concentration not lower than 0·1 molar. Measurements of the *E.M.F.* of cells of the above type are given at 18°, 25°, and 35° with HCl concentrations from 0·033 to 4·5

molar. From these values have been computed: (1) The change in free-energy content and in heat content attending the reaction H_2 (1 atm.) + Hg_2Cl_2(solid) = 2Hg(liquid) + 2HCl at various concentrations; (2) the change in free-energy content and in heat content attending the change HCl(at c_1) = HCl(at c_2); (3) the ratio of the activities of the hydrogen ion or chloride ion in solutions of various concentrations. With the aid of data obtained by Jahn for the *E.M.F.* of concentration cells at 18°, the series of free-energy values is extended to HCl concentrations down to 0·00167 molar. Further, combining these results with calorimetric data, it has been possible to determine the absolute free energy of HCl (referred to the free energies of the elements as zero) at 18°, 25°, and 35°, in solutions from 0·00167 to 4·5 molar.

Assuming that at the lowest concentration (0·00167 molal) the ion activity is equal to the ion concentration, a series of absolute activity coefficients for HCl in solution has been computed. These are compared with activity-coefficients calculated for potassium chloride from *E.M.F.* measurements and from osmotic pressure data. The conclusion is drawn that the activity-coefficients, both of hydrochloric acid and of potassium chloride, decrease up to concentrations of 0·1 molar far more rapidly than do the conductance-viscosity ratios. The difference amounts to 9% for hydrochloric acid and 15% for potassium chloride at this concentration, so that in using the conductance ratio as a measure of ion activity in mass-action expressions a corresponding error is involved. At a concentration of 0·5 molar the activity-coefficient of hydrochloric acid reaches a minimum, and then increases very rapidly with increasing concentration, becoming 2·23 times as great at 4·48 molar as at zero concentration.

It is further shown that the activity-coefficients of potassium chloride derived independently from *E.M.F.* and from freezing-point measurements agree very closely, affording evidence that for this salt the conductance ratio is a true measure of ion concentration (although not of ion activity), as is assumed in making the calculation from the freezing points. E. H. R.

Cathode-scattering in Electrolysis. A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1374—1384).—If a current is passed through a solution of sodium hydroxide or dilute sulphuric acid in contact with a lead cathode, and the current density is not too small, cathode-scattering occurs. The dependence of this scattering on the nature and concentration of the electrolyte, the current density, and the temperature has been quantitatively examined.

Preliminary measurements showed that the amount of scattering varied considerably with the purity of the lead and that low results were obtained with a new cathode or a fresh solution. Although these effects are as yet unexplainable, it has been found possible to eliminate their influence in the comparative experiments the results of which are recorded.

The scattering in solutions of sodium hydroxide, carbonate,

and sulphate increases with increase in the current density, rapidly at first, then much more slowly, and approaches to a constant limit. According to experiments with solutions of sodium carbonate, the scattering increases with falling concentration and with falling temperature. Potassium salts behave very much the same as sodium salts, but with calcium salts the scattering is relatively very slight. The effect is considerable in 0·01 and 0·1*N*-sulphuric acid at higher current densities. As the concentration of the acid increases the scattering diminishes, and vanishes in 0·5*N*-solution.

In explanation of the observations, it is supposed that the scattering in the alkali hydroxide and salt solutions is mainly due to the formation of an alloy of lead with the alkali metal, the secondary decomposition of this by the water leading to the formation of finely divided lead. In acid solution, the scattering is of a different type, and it is suggested that discharged hydrogen atoms penetrate into the cathode, where they combine to form molecular hydrogen, which in its escape from the metal produces the scattering effect. H. M. D.

Coefficients of Expansion of Gases. Applications. Internal Pressure and Internal Work. The Experiments of Kelvin and Joule. Perfect State of True Gases. A. LEDUC (*Ann. Physique*, 1916, [ix], **5**, 180—217).—A more detailed mathematical discussion of work already published (compare A., 1909, ii, 298, 381, 382, 542, 550, 644; 1911, ii, 792). W. G.

The Specific Heat at Low Temperatures. III. Measurements of the Specific Heat of Solid Nitrogen between 14° (Absolute) and the Triple Point, and of Liquid Nitrogen between the Triple Point and the Boiling Point. W. H. KEESOM and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1247—1255).—The atomic heat of solid nitrogen increases from 1·60 at 15·27° (abs.) to 5·48 at 61·68° (abs.). The temperature variation of the atomic heat differs considerably from that which is found in the case of monatomic solid substances, and it is inferred that nitrogen in the crystalline condition is diatomic.

The atomic heat of liquid nitrogen is about 6·7 between 64° and 76° (abs.). This is considerably greater than the value 6·0 obtained by Alt (A., 1904, ii, 393). H. M. D.

Binary Mixtures. III. Freezing-point Curves. ARTHUR BRAMLEY (T., 1916, **109**, 469—496).—In the further investigation of the constitution of mixtures of phenols and bases, measurements have been made of the freezing points of some of the pairs of substances the viscosity of which has been investigated in the two previous papers (see this vol., ii, 125, 376).

According to the freezing-point curves, phenol and quinoline form two compounds, $(C_6H_5{\cdot}OH)_2,(C_9H_7N)_3$ and

$$(C_6H_5{\cdot}OH)_2,(C_9H_7N).$$

With pyridine, phenol also forms two compounds,

$$(C_6H_5{\cdot}OH),(C_5H_5N) \text{ and } (C_6H_5{\cdot}OH)_2,(C_5H_5N).$$

The curves for mixtures of phenol with dimethylaniline and with diphenylmethylamine consist of two branches meeting in the eutectic point.

The curves for mixtures of the three cresols with pyridine show that *o*-cresol forms the compound $(C_7H_8O),(C_5H_5N)$ and *p*-cresol the same, as well as the compound $(C_7H_8O)_2,(C_5H_5N)$. Mixtures of *m*-cresol and pyridine containing from 35 to 75 mols. % of the cresol could not be made to crystallise, and the question of the combination of these substances remains unsolved so far as freezing-point evidence is concerned.

The curves for mixtures of *o*-chlorophenol with various bases show that the phenol combines with aniline, dimethylaniline, pyridine, quinoline, and acetone to form compounds which contain the components in the ratio 1 : 1. For mixtures of *o*-chlorophenol and diphenylmethylamine two intersecting curves are obtained, and there is consequently no evidence of compound formation.

When the freezing-point curves are compared with the corresponding viscosity curves, it is found that in some cases both series of measurements lead to the same conclusion, whilst in others the results appear to be at variance. For certain binary mixtures, compound formation is indicated by viscosity measurements and not by the freezing-point curves, and, on the other hand, there are pairs of substances for which the formation of compounds is clearly indicated by the freezing-point diagrams, but is not suggested by the viscosity curves. In most cases, however, when the formation of a compound is not indicated by the freezing point the viscosity curve is sagged, and when the freezing-point diagram affords evidence of compound formation the viscosity curve lies wholly or in part above the straight line corresponding with the simple mixture rule. H. M. D.

Binary Mixtures. IV. Heats of Reaction and Specific Heats. ARTHUR BRAMLEY (T., 1916, **109**, 496—519).—On account of the apparently contradictory evidence afforded by viscosity curves and freezing-point diagrams for some of the binary mixtures examined in the previous papers (compare preceding abstract), further information has been sought by a study of the specific heats of mixtures of phenols and bases, and also of the heat changes which occur when the components are mixed in various proportions.

A vacuum-jacketed form of Bunsen ice calorimeter was employed for the thermal measurements, whereby the determination of the heats of reaction was not affected by the question of the specific heats. The specific heats were measured in all cases between 0° and 20°, and for some mixtures between 0° and 100°.

The mixtures examined were *o*-cresol and pyridine, *m*-cresol and pyridine, and mixtures of *o*-chlorophenol with dimethylaniline, quinoline, pyridine, acetone, and diphenylmethylamine.

With one exception, these mixtures are characterised by the development of considerable quantities of heat, and this may be regarded as strong evidence of the formation of compounds. The

exception is represented by mixtures of *o*-chlorophenol and diphenylmethylamine, which show a relatively small absorption of heat. The curves which are obtained by plotting the heat of reaction as a function of the composition show a well-developed maximum. The composition corresponding with this maximum is in general appreciably different from that of the equimolecular mixture, but this may be explained when it is considered that the observed heat of reaction is the algebraic sum of the heat effects due to the formation of compound molecules and the dissociation of complex molecules of the components. When the disturbing effect of dissociation is taken into account, the heats of reaction may be said to afford evidence of the formation of the equimolecular compound in all the mixtures examined, with the exception of *o*-chlorophenol and diphenylmethylamine. By application of the law of mass action to the equilibrium between the compound and its components, and by assuming that the amount of the compound formed is proportional to the heat of reaction, it is possible to calculate the equilibrium constant from the thermal data for two different mixtures. For mixtures of *o*-chlorophenol and quinoline, the value so obtained indicates that the components in the equimolecular mixture are combined to the extent of about 87%. It is not claimed that this is more than a rough approximation to the true value. H. M. D.

Liquid Chlorine as a Solvent. Cryoscopic Determinations at Low Temperatures. P. WAENTIG and D. McINTOSH (*Trans. Roy. Soc. Canada*, 1916, **9**, [3], 203—209).—Cryoscopic determinations in liquid chlorine were made in a silvered Dewar flask fitted with a rubber stopper carrying a tube which served as an air chamber for the freezing-point tube. The desired temperatures ($-105°$ to $-108°$) were obtained by means of solid carbon dioxide and ether boiling under reduced pressure. Temperatures were measured by means of a platinum thermometer and a Carey-Foster bridge. Determinations with substances unlikely to form compounds with chlorine, such as toluene, chloroform, carbon tetrachloride, and stannic chloride, gave as a mean value for K 28·8, from which the latent heat of solid chlorine, calculated by the van't Hoff equation, is 20·4 cal. per gram. Determinations with ethyl ether and ethyl acetate, which form compounds with the halogens of the type $C_4H_{10}O,X_2$ and $CH_3{\cdot}CO_2Et,X_3$, show normal results, indicating that the compounds are broken down in solution. Acetone is polymerised in concentrated solutions, whilst ethyl and methyl alcohols are greatly associated at all dilutions. Water and iodine do not change the freezing point of chlorine, and hence are either insoluble or very slowly soluble in liquid chlorine. Bromine raises the freezing point. G. F. M.

Maximum Vapour Pressures of Camphor at Moderate Temperatures. P. DATIN (*Ann. Physique*, 1916, [ix], **5**, 218—240). —A comparison of the ordinary barometric method and the method of evaporation (compare Allen, T., 1900, **77**, 400, 413) for

measuring vapour pressures where the values are small. The comparison was made using camphor purified by sublimation. The barometric method becomes more precise as the maximum pressure increases, the order of accuracy depending on the cathetometer used. The method of evaporation is preferable to the barometric method for the measurement of maximum vapour pressures below 2 mm. of mercury, and in order to obtain accurate results it is advisable to allow the evaporation to proceed for a considerable length of time. Results obtained with purified, synthetic, and commercial camphors are shown in graphic form over a temperature range of 18—80°, the values obtained for pure, resublimed camphor being slightly higher than those found by Allen (*loc. cit.*). W. G.

The Consequences of the Comparison of Reversible Solutions with Saturated Vapours. ALB. COLSON (*Compt. rend.*, 1916, **162**, 753—756. Compare *ibid.*, 122).—A theoretical discussion of the similarity between the conditions governing reversible solutions and saturated vapours when Clapeyron's formula is applied to each case, in which the author adduces further arguments in support of the conclusions previously drawn by him (compare A., 1915, ii, 823). W. G.

Complete Expression for the Heat of Reversible Solution in a Volatile Liquid. C. RAVEAU (*Compt. rend.*, 1916, **162**, 756—757).—A mathematical consideration of the subject. W. G.

Determination of Ring-tension from Thermal Data. P. E. VERKADE (*Chem. Zentr.*, 1916, i, 205—206; from *Handelingen van het Vijftende Natuur*, 1915, 9).—The heat of hydration of a number of dibasic acid anhydrides was found to be almost identical with the change in the heat of combustion involved by the replacement of 2OH by O, hence the energy of ring formation is practically zero, whence the conclusion is drawn that in 5- and 6-ring carbon–oxygen systems there is practically no tension. The heats of combustion of a number of *cyclo*methylene compounds and the corresponding open-chain compounds were determined. The introduction of a methyl group into an open-chain hydrocarbon raised the heat of combustion by about 157·5 cal. Since the same value was obtained with *cyclo*pentane, *cyclo*hexane, and *cyclo*heptane and their monomethyl derivatives, there can be no tension in these compounds due specially to ring formation. The tension in the smaller rings, *cyclo*propane, etc., amounts to 20—30 cal. These results stand in direct contradiction to Baeyer's tension theory. The following values are given for the heats of combustion of the undermentioned acids and their anhydrides: benzoic acid, 772·0; anhydride, 1556·3; cinnamic acid, 1049·9; anhydride, 2092·4; diphenylacetic acid, 1649·9; anhydride, 3309·6; diethylacetic acid, 830·6; anhydride, 1668·7; heptoic acid, 985·7; anhydride, 1984·8. Reduced hydration constants (hydration constants less the influence

of the dissociation constants of the acids), K_r^{25} of succinic anhydride, 0·0107; maleic anhydride, 0·0009; methylsuccinic anhydride, 0·0112; itaconic anhydride, 0·0065. G. F. M.

Supposed Effect of the Form of Container on the Density of a Gas. WILLIAM A. NOYES and LAURENCE C. JOHNSON (*J. Amer. Chem. Soc.*, 1916, **38**, 1017—1021).—In determinations of the volumetric ratio in which oxygen and hydrogen combine, Morley obtained a mean value 1:2·00023, whilst Scott found the ratio to be 1:2·00285. In neither case did the probable error exceed 1 part in 25,000. Since, in the former experiments, the gases were measured in a eudiometer tube and in the latter in spherical vessels, Morley has suggested that the discrepancy may be due, in some way, to the difference in the shape of the vessels. Comparison has therefore been made of the volume occupied by a gas in a system of tubes with that which it occupies in a bulb, and it has been found that the difference does not exceed 1 part in 10,000, whereas Morley and Scott's determinations differ by 1 part in 1000. E. G.

The Effect of Unsaturation on the Molecular Volumes of Organic Compounds. GERVAISE LE BAS (*Chem. News*, 1916, **113**, 253—255).—Molecular volumes are recorded in support of the view that the volume occupied by two atoms of hydrogen is equal to the difference between the volumes of an ethenoid compound and the corresponding saturated compound. In unsaturated compounds which contain an acetylene linking or two ethenoid linkings, the removal of the second pair of hydrogen atoms is accompanied by a slight increase in volume. A similar effect is shown when a relatively small atom like chlorine is replaced by larger atoms, such as bromine and iodine.

A comparison of the molecular volumes of benzene derivatives with those of di-, tetra-, and hexa-hydrobenzene derivatives affords evidence in support of the view that the extra hydrogen atoms in the reduction products resemble the hydrogen atoms in saturated aliphatic compounds in their volume relations. H. M. D.

Further Study of Floating Equilibrium. THEODORE W. RICHARDS and GORHAM W. HARRIS (*J. Amer. Chem. Soc.*, 1916, **38**, 1000—1011).—In earlier papers (A., 1912, ii, 599; 1914, ii, 98) it has been shown that the method of floating equilibrium can be applied to the analysis of solutions, the calibration of thermometers, and the determination of coefficients of expansion. The present paper describes experiments relating to the precautions required for quick and accurate determination of the floating equilibrium, the thermal hysteresis of glass floats, the influence of changes of pressure on the behaviour of the floats, and the effect of traces of common impurities in water. Concentration-temperature curves have been studied with several floats made of different kinds of glass in dilute hydrochloric acid, and it is shown that such curves can be employed for estimating hydrochloric acid in

solution or for the approximate standardisation of a given interval in a thermometer. The almost identical coefficients of expansion of very dilute solutions render such a curve an expression of the relation between the density of any very dilute solution and the temperature of floating equilibrium, and thus enable densities to be determined thermometrically. E. G.

Compressibility of Certain Typical Hydrocarbons, Alcohols, and Ketones. T. W. RICHARDS and J. W. SHIPLEY (*J. Amer. Chem. Soc.*, 1916, **38**, 989—999).—The present work on the compressibility of organic compounds was carried out in continuation of that already published (A., 1909, ii, 214; 1912, ii, 896, and earlier papers). The same method was adopted as in the earlier work, but the pressure gauge and piezometer were improved, and a study was made of the pressure-volume hysteresis of glass. The compressibility of the following compounds is recorded in terms of megabars over the ranges 100—300 megabars and 300—500 megabars: methyl alcohol, ethyl alcohol, acetone, diethyl ketone, $\beta\epsilon$- and $\beta\delta$-dimethylheptanes, benzene, toluene, ethylbenzene, *iso*- and *n*-propylbenzenes, *tert.*-butylbenzene, mesitylene, ψ-cumene, *cyclo*hexane, *cyclo*hexanol, and *cyclo*hexanone. The experiments were conducted at 20°, except in the case of liquid *cyclo*hexanol, in which determinations were made at 40° and 34°.

The results show a remarkable parallelism between the change of compressibility with pressure and the magnitude of the compressibility itself; in nearly all cases greater compressibility is accompanied by greater change of compressibility under increasing pressure. They also indicate that in a given series of compounds the more compressible substance has the lower b. p. E. G.

Binary Mixtures. II. The Densities and Viscosities of Mixtures Containing Substituted Phenols. ARTHUR BRAMLEY (T., 1916, **109**, 434—469. Compare this vol., ii, 125).—The investigation of binary mixtures of phenol with bases of varying strength has shown that the chemical combination of the components of the mixtures tends to make the viscosity greater than that calculated from the simple mixture rule. The anomalous results obtained with certain pairs of substances have been attributed to molecular association of one of the components, and in order to test the validity of this hypothesis, further measurements have been made in which the phenol was replaced (1) by substituted phenols differing only in the degree of molecular association, and (2) by non-associated phenols of more strongly acidic nature. As in the investigation of the phenol mixtures, the measurements of viscosity and density were made over a wide range of temperature.

The results obtained for mixtures of the three cresols and phenol with pyridine show that *o*-cresol differs considerably from the three other phenols in so far as the viscosity relations of these mixtures are concerned. It seems probable that molecular association is the factor which is mainly responsible for this difference, the associa-

tion factor for *o*-cresol (1·09) being much smaller than the value for phenol (1·30), *m*-cresol (1·41), or *p*-cresol (1·44). The same sequence is obtained if the phenols are arranged according to the temperature at which the viscosity curves for the pyridine mixtures begin to show a maximum. The temperatures in question are: *o*-cresol, 3°; phenol, 45°; *m*-cresol, 67°; *p*-cresol, 74°.

The viscosity curves for mixtures of *o*-chlorophenol with aniline, dimethylaniline, quinoline, and pyridine are characterised by a well-developed maximum. The curves for mixtures of *o*-chlorophenol with diphenylmethylamine are of the sagged type, and sinuous curves are obtained for mixtures of *o*-chlorophenol and acetone.

Experiments with the much more strongly acidic *o*-nitrophenol gave viscosity-composition curves showing a maximum with quinoline, and a minimum with aniline, whilst the curves for pyridine mixtures are sagged. In spite of its more pronounced acidity, *o*-nitrophenol appears to combine with bases to a much smaller extent than *o*-chlorophenol, and it is suggested that this may be due to the greater dissociating power of the nitro-compound as measured by its dielectric constant.

The observations show that any change in the binary mixture which tends to increase (decrease) the complexity of the molecular condition gives rise to an increase (decrease) in the viscosity. For many apparently indifferent pairs of substances, sagged viscosity curves are obtained, and this is to be attributed to the dissociating effect of the components on one another. When chemical combination occurs, the difference between the observed viscosity and that calculated by the mixture rule should be a maximum for the mixture which contains the largest proportion of the compound formed. This is very frequently found not to be the case, and such deviations must be attributed to the disturbing influence of the molecular association of the components and their unequal dissociating power. On account of these disturbing factors, measurements of the viscosity of mixtures cannot be regarded as a trustworthy test of compound formation, and still less can it be regarded as a safe method of determining the composition of such compounds. H. M. D.

Osmotic Pressure of Colloidal Hydrated Ferric Oxide. F. VAN DER FEEN (*Chem. Weekblad*, 1916, **13**, 453—458).—An account of determinations of the osmotic pressure of colloidal solutions of hydrated ferric oxide. A. J. W.

Relation of Osmosis of Solutions of Electrolytes to Membrane Potentials. Theoretical. F. E. BARTELL and CARL D. HOCKER (*J. Amer. Chem. Soc.*, 1916, **38**, 1029—1036).—The osmosis of solutions of electrolytes shows a close relationship to the differences of potential between the two faces of membranes separating such solutions from water, and this fact supports the view that the osmosis of such solutions is largely dependent on the electrical condition of the membrane. Theoretical considera-

tions are advanced which support the view that the osmotic effects observed in the experiments already described (A., 1914, ii, 347) can be best explained by the following assumptions.

The abnormal osmosis is due primarily to an electrical effect, and is analogous to electrical osmosis. The osmosis of the solutions is due to the passage of a charged liquid layer along the capillary tubes of the membrane under the driving force of a difference of potential which acts as though it were set up between the two faces of the membrane. The charge on the movable liquid layer is determined by the charge which the porcelain assumes when immersed in water, but this charge may be altered by selective adsorption of ions when the membrane is brought into contact with solutions of electrolytes; and other ions than those of hydrogen and hydroxyl may affect the charge on the membrane. The polarisation of the membrane is probably determined by the relative rates of diffusion of the ions through the membrane, but may be altered by other factors, such as ionic adsorption. The extent of osmosis may be affected by the relative volumes of water and salt solution on the two faces of the membrane, since this factor may affect the diffusion of the salt through the membrane. E. G.

Osmosis of some Solutions of Electrolytes with Porcelain Membranes, and the Relation of Osmosis to Membrane Potential. F. E. Bartell and Carl D. Hocker (*J. Amer. Chem. Soc.*, 1916, **38**, 1036—1050).—Bartell (A., 1914, ii, 347) has shown that some salt solutions when placed in osmotic cells constructed of porcelain membranes of certain grades gave negative osmosis, that is, the direction of the flow of liquid was from the concentrated to the more dilute solution. The present work was undertaken to study the relation of osmosis to membrane potential and to determine the manner in which the osmosis varies with the concentration of solutions of electrolytes and with the diffusion of such electrolytes from the cells.

Cells were constructed of porcelain membranes of such porosity that the diameter of the largest pores was about 0·2 micron, and the osmosis of the following electrolytes was investigated: solutions of various nitrates of concentrations varying from 0·0005M to M; solutions of various potassium salts of concentration 0·1M; solutions of hydrochloric acid and of sodium hydroxide of concentrations between 0·001M and 0·2M; and 0·1M solutions of some typical nitrates when the membranes were immersed in hydrochloric acid and in sodium hydroxide of different concentrations.

It was found that the osmosis of these electrolytes varies in different ways with the concentration. Some give positive effects, which increase with the concentration of the electrolyte; others give positive effects at low concentrations and negative effects at higher concentrations, the positive osmosis decreasing as the concentration of the electrolyte is increased. For some electrolytes there is a particular concentration which gives the maximum positive osmosis, whilst other concentrations, both higher and lower, give smaller positive effects; and for others there is a con-

centration which gives the greatest negative osmosis, whilst all other concentrations give effects tending to be more positive. In the case of all the nitrates, except those of aluminium and thorium, a concentration was found at which the effect was practically zero. Osmosis seems to be closely related to the electrical orientation of the membrane and to the difference of potential between the solutions bathing the faces of the membrane. In most cases the orientation of the membrane is that which would be expected from the difference in migration velocities of the ions, without considering the membrane, but in a few cases it is the reverse. In the case of all the monobasic salts, the greater the rate of diffusion of salt through the membrane the greater is the positive osmosis. The rate of diffusion is always closely related to the magnitude of the cell potential. E. G.

The Calculation of the Dissociation Constants of Extremely Weak Acids and Bases. KARL H. A. MELANDER (*Biochem. Zeitsch.*, 1916, **74**, 134—136).—The author has recalculated the formula for the dissociation constant of an acid determined by the measurement of the change of the hydroxyl (or hydrogen) ion concentration when a given amount of acid is added to a given solution of alkali hydroxide. It is $k = \gamma . [\overset{+}{H}] . \Delta_{\bar{OH}}/[S] - \Delta_{\bar{OH}}$, where S is the concentration of the added acid, $\Delta_{\bar{OH}}$ is the change produced in the hydroxyl-ion concentration of the alkali due to addition of the acid, and γ is the dissociation grade of the sodium salt of the acid, that is, $[\bar{S}]/[\bar{S}] + [NaS]$, $[\bar{S}]$ being the concentration of the acid ions. S. B. S.

The Entropy of Solid Solutions. OTTO STERN (*Ann. Physik*, 1916, [iv], **49**, 823—841).—A theoretical paper in which the author shows that it is probable that the entropy of solid solutions converges to a zero value with falling temperature, as required by Nernst's theorem. H. M. D.

Mode of Attachment of the Water of Imbibition in Crystals which are Capable of Swelling in Water. J. R. KATZ (*Zeitsch. physiol. Chem.*, 1915, **95**, 1—15).—The author has measured the changes in the vapour pressure of crystals of carboxyhæmoglobin from the blood of the horse and of the dog, of vitellin from pumpkin seeds, of Bence-Jones albumose, and of amylodextrin, corresponding with the changes in the amounts of water of imbibition contained in them. The estimation of the vapour pressure was carried out by exposing a small quantity of the crystals in a desiccator containing a mixture of water and sulphuric acid of known vapour pressure until the weight was constant, the amount of water in the crystals being then ascertained. On plotting the vapour pressures against the corresponding water-contents, regular curves are obtained in each case without any discontinuities, which indicates that the water and the carbohydrate, protein, or lipoid, as the case may be, form a solid solution and constitute a particular case of "mixed crystal." All the substances examined

retained their crystalline condition during the imbibition of the water, although the characteristic angles altered owing to imbibition occurring in certain directions to a greater extent than in others. H. W. B.

Mode of Attachment of the Water of Imbibition in Hæmin Crystals. J. R. KATZ (*Zeitsch. physiol. Chem.*, 1915, **95**, 16—17. Compare preceding abstract).—Hæmin crystals were dried at 130° in a current of nitrogen, and the changes in vapour pressure corresponding with changes in the content of water of imbibition estimated by the method indicated in the preceding abstract. The curve showing the relation between the water-content of the crystals and the vapour pressure is continuous, indicating the existence of a state of solid solution of the water in the hæmin and the absence of true water of crystallisation. H. W. B.

The Relation between the Angles of Mixed Crystals and those of their Components. FERRUCCIO ZAMBONINI (*Compt. rend.*, 1916, **162**, 835—837).—The molybdates of calcium, strontium, and lead form mixed crystals with the corresponding salts of cerium, didymium, and yttrium. These have been examined goniometrically, and the values of angles between pyramid faces on crystals of the simple salts and of mixed crystals are recorded. In almost every case it is found that the size of this angle does not bear any simple relation to the composition of the mixed crystals, and in some cases its value does not even lie between the values of the corresponding angle on crystals of the simple components. E. H. R.

Liesegang's Rings and Related Phenomena. IV. The Morphological Characters of Liesegang's Rings. ERNST KÜSTER (*Kolloid Zeitsch.*, 1916, **18**, 107—116. Compare A., 1913, ii, 893; 1914, ii, 630).—The ring structures which are developed when certain substances react in a gelatin medium are analysed, and the phenomena of rhythmic crystallisation discussed. H. M. D.

Hydrosols of Mercury and of its Oxygen Compounds. CONRAD AMBERGER (*Kolloid Zeitsch.*, 1916, **18**, 97—101).—Many substances which act as efficient protective colloids towards metals like silver, platinum, and palladium in the hydrosol condition are found to be relatively ineffective in the case of colloidal mercury. Such preparations as have been obtained change more or less rapidly on keeping, and the mercury becomes insoluble.

It has been found that stable, therapeutically active, colloidal mercury can be obtained by the use of albumins or their products of decomposition as protective agents. Solid hydrosols containing up to 80% of mercury have been prepared by the addition of a solution of mercuric chloride to mixtures of glutin or dextrin with pyrogallol, catechol, or certain aminophenols, whereby a yellowish-white precipitate is obtained. On the addition of alkali reduction takes place, and colloidal mercury is obtained.

If glutin or dextrin is mixed with a solution of an alkali and a mercuric salt added, colloidal mercuric oxide is obtained. By the reaction of colloidal mercury with colloidal mercuric oxide, prepared as described above, stable preparations of colloidal mercurous oxide are obtained. H. M. D.

Non-, Uni-, and Bi-variant Equilibria. VII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1384—1398. Compare this vol., ii, 231).—A further discussion of the relations exhibited by pressure-temperature equilibrium diagrams. H. M. D.

The Pressure-composition Diagrams of Unary Systems according to the Theory of Allotropy. A. SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1334—1350).—A theoretical paper in which the author discusses the equilibrium relationships in so-called pseudo-unary systems on the hypothesis that the various solid (enantiotropic, monotropic) phases consist of at least two kinds of molecules in internal equilibrium. H. M. D.

Suggestion Concerning the Statement of the Phase Rule. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1916, **38**, 983—989).—The chief difficulty encountered by beginners in connexion with the phase rule is with regard to the definition of the term "component." It is therefore suggested that the idea of the component should be replaced by that of the "individual," which is defined as follows: "the individuals of any reacting system are the separate chemical substances, undecomposed in the reactions concerned, which are necessary to construct the system; the number of such individuals to be chosen is the smallest number necessary to construct the system." Into the equation, representing the phase rule and expressing the number of degrees of freedom, a term is introduced giving the maximum number of independent restrictions involved in the fixation either (1) of one or more of the intensity factors of the forms of physical energy concerned, or (2) of some concentration relation of the individuals in the variable phase. An outline is given of an inductive method of evolving the phase rule for beginners. E. G.

The Ignition of Mixtures of Methane and Air and Hydrogen and Air by means of the Impulsive Electric Discharge. SOSALE GARALAPURY SASTRY (T., 1916, **109**, 523—529).—Recent observations on the electrical ignition of gas mixtures (Thornton, A., 1914, ii, 524, 834; 1915, ii, 734) have led to the view that continuous alteration of the proportions of gas and air in an explosive mixture is, or may be, accompanied by discontinuous alterations in the energy of the igniting spark. In order to check the observations which have led to the theory of stepped ignition, further experiments have been made with mixtures of methane and air and with mixtures of hydrogen and air. It was found that comparable results could only be obtained when precautions were taken to

ensure constancy of the rate of break of the primary circuit of the induction coil used for the production of the single disruptive discharges and also constancy in the condition of the secondary spark-gap. It is probable that the relative energies required for the ignition of different mixtures are proportional to the minimum currents in the primary of the induction coil which, when broken, cause ignition, and the curves, which are obtained when these minimum igniting currents are plotted against the composition of the gas mixtures, are perfectly continuous. There is consequently no support for the theory of stepped ignition. H. M. D.

Influence of some Solvents on the Rate of Action of Sodium with *iso*Amyl Bromide. PAUL WHITTIER CARLETON (*J. Amer. Chem. Soc.*, 1916, **38**, 1128—1136).—Experiments are described which were carried out with the object of determining the rate of reaction of sodium (in particles with an average diameter of 0·1—0·2 mm.) with *iso*amyl bromide, dissolved in ether, in dimethylaniline, and in benzene. The reaction proceeded more rapidly in ether than in benzene, and much more rapidly in dimethylaniline than in either of the other two solvents. This cannot be explained as a result of the dissociation of the *iso*amyl bromide, but is regarded as due to the formation of ammonium salts and, to a slight extent, to the formation of oxonium salts, and to the replacement of the less positive basic organic radicle in the salt by sodium. The effect of certain impurities on the rate of reaction was investigated, and it was found that small quantities of alcohol or acetone cause a very great acceleration. E. G.

The Velocity of Coagulation of Aluminium Hydroxide Solution. JOHN A. GANN (*Koll. Chem. Beihefte*, 1916, **8**, 63—138).—The rate of coagulation of colloidal aluminium hydroxide in presence of various salts of the alkali metals has been examined with the view of elucidating the chief factors which influence the velocity of the process. The progress of coagulation was followed by measurement of the change in the viscosity of the solutions.

The results obtained show that the coagulation is an auto-catalytically accelerated process, which, in the case of the more dilute colloidal solutions, takes place in accordance with the equation $dx/dt = k_1(1 + b_1x)(1 - x)$, where x is the increase in the viscosity after time t, expressed as a fraction of the total increase, and k_1 and b_1 are constants. For univalent anions of various kinds, the total change in the viscosity has the same value. For more concentrated solutions of aluminium hydroxide, the progress of coagulation approximates more closely to that expressed by the formula $dx/dt = k_1'(1 - x)^2$.

The coefficient k_1 varies but little with the concentration of the colloid, and b_1 is nearly independent of the nature and concentration of the anion of the coagulating electrolyte. On the other hand, k_1 increases rapidly with the concentration of the electrolyte, the relation being expressed by the exponential equation $k_1 = kc^p$, in which p is approximately equal to 5. In view of this relation,

it is evident that the range of concentration over which the velocity of coagulation can be measured for a given electrolyte is very limited, and that a particular concentration can be assigned to each electrolyte which represents the lowest concentration which causes coagulation with measurable velocity. These concentrations, or more accurately those which correspond with the same value of k_1, may be taken to represent the coagulating powers of the various electrolytes concerned.

The coagulating power depends on the valency and nature of the anion, and in agreement with views previously put forward by Freundlich it is found that the coagulating concentrations are those which correspond with equivalent quantities of the adsorbed anions. In proof of this relation, measurements were made of the quantities of various alkali salts which are adsorbed by aluminium hydroxide.

The viscosity of a colloidal aluminium hydroxide solution increases with the concentration according to a linear equation, but the increase is much more rapid in the case of the coagulated sol. The relations involved depend to a considerable extent on the method of measuring the viscosity. H. M. D.

Chemical Reactions in Anisotropic Liquids. II. THE. SVEDBERG (*Kolloid Zeitsch.*, 1916, **18**, 101—106. Compare this vol., ii, 211).—Measurements of the rate of decomposition of picric acid, trinitroresorcinol, and pyrogallol in an anisotropic solvent have shown that the reaction velocity is diminished when the solution is subjected to the influence of a magnetic field. The solvent used was *p*-azoxyphenetole, the temperature of measurement 140°, and the progress of the reaction was followed by determining the electrical conductivity of the solutions. The effect was not observed in similar experiments with maleic acid as the dissolved substance. H. M. D.

Catalysis of Hydrogen Peroxide in Heterogeneous Media. Experiments with Oxides. GEORGES LEMOINE (*Compt. rend.*, 1916, **162**, 702—708. Compare A., 1912, ii, 747; 1915, ii, 626).—A quantitative study of the effect of a number of oxides on the decomposition of hydrogen peroxide. The value of n in the equation $y/p=k(1-y/p)^n dt$, where p is the weight of real hydrogen peroxide in 1 gram of the starting liquid, and y is the weight decomposed in the time t, n and k being constants, has been determined in each case. Freshly precipitated ferric oxide dried at 180° exerts a more energetic catalytic effect at 21° than at 69·5°, and calcination of this oxide for twenty minutes at a red heat reduces its catalytic effect. The value $n=2$ was obtained in each case. The more compact oxide, colcothar, is an efficient catalyst, but less energetic than the two previous oxides. The value of n is 1. The catalysis increases with the weight of oxide taken, but not proportionally. Aluminium oxide is a negative catalyst, the value of n being 1. Cerium oxide is an excellent catalyst, and gives $n=2$. Calcined silica is a more effective catalyst than dried silica. The catalysis in both cases increases rapidly with the weight. Thorium

oxide when used in sufficient quantity increases the decomposition of the hydrogen peroxide, but there was indication that in small quantities it acted as a negative catalyst. The value of n is 1.

W. G.

Catalysis of Hydrogen Peroxide in Heterogeneous Media. Experiments with Carbon; Conclusions. GEORGES LEMOINE (*Compt. rend.*, 1916, **162**; 725—731. Compare this vol., ii; 308, 309, preceding abstract).—Of the three types of charcoal tried, namely, from cocoa-nut, from wood, and from sugar, all three are efficient catalysts for the decomposition of hydrogen peroxide, the most energetic being cocoa-nut charcoal. Their function as catalysts is apparently correlative with their absorptive power for gases. The value of n in the equation (*loc. cit.*) was in each case 2. The catalysis by means of charcoal was similar to that with platinum moss. A series of experiments was performed, using charcoal charged with various gases, and it was found that the nature of the gas had little, if any, influence on the catalysis. The catalytic effect was relatively much greater at 15° than at 33°. The velocity of decomposition increased in every case with the weight of catalyst used, but not proportionately.

W. G.

The Hardening of Fats. W. NORMANN (*Chem. Zeit.*, 1916, **40**, 381—383).—A reply to the contentions of Siegmund and Suida (A., 1915, ii, 626) and of Erdmann (A., 1915, i, 770), that the hardening of fats is not necessarily conditioned by the presence of metallic nickel. The author, after introductory remarks of a polemical character on the history of the fat-hardening process, denies Erdmann's suggestion that the presence of free nickel in the oxide catalyst after use was due to a reduction by impurities in the oil or to the employment of temperatures higher than 250—260°. Further, the carbonyl reaction with which a positive result was obtained is perfectly trustworthy, as blank experiments, even at 90°, with nickel oxides, failed to give any nickel mirror, and the experiments in question were carried out at far lower temperatures than this, and still indicated the presence of metallic nickel in the catalyst. The presence of carbon dioxide in the emerging carbon monoxide is no indication of the reduction of nickel oxides by the latter gas, since the monoxide is itself resolved into carbon and carbon dioxide by the catalytic action of metallic nickel. The conductivity measurements of Siegmund and Suida are regarded as untrustworthy, if only on account of their own lack of agreement, which is to be attributed to the organic substances present in the used catalyst. Electrical conductivity depends essentially on the form, situation, and state of division of the metallic particles, rather than on the actual amount of metal present, and the fact that Erdmann found conductivity by adding 5% of reduced nickel in comparatively coarse particles to a catalyst which previously was not conducting, is no proof of the previous absence of free nickel. The author's original experiments with Pungs have now, moreover, been confirmed, using a synthetic

triolein of undoubted purity, and hardening at 250°, the process being stopped while the fat was still liquid. The catalyst was then separated, and gave the carbonyl reaction at 50°, and showed electrical conductivity with the greatest facility. It is, therefore, considered that metallic nickel is certainly present in quite sufficient quantity to account for the catalytic action, and it is unreasonable to wish to ascribe to a hypothetical nickel suboxide an effect which is amply accounted for by a substance which is positively shown to be present, and is known to be capable of exerting that effect.

G. F. M.

Errors Affecting the Determination of Atomic Weights. I. The Weighings. PH. A. GUYE (*J. Chim. phys.*, 1916, **14**, 25—54).—A theoretical paper in which the errors affecting atomic weight determinations are considered. The present paper deals particularly with the errors which may occur in the weighings. These are considered under the headings of: (i) the balance; (ii) the weights; (iii) the apparatus weighed; and (iv) the reduction of the weight to vacuum standard. The main causes of error in the weighings are: (i) difference between the temperatures of the air above the pans of the balance; (ii) use of weights which have screwed-on heads; (iii) inaccuracies due to calibration of brass weights with platinum weights; (iv) occlusion of gas or formation of water particles on the surface of weights (particularly platinum weights); (v) differences in volume between the apparatus weighed and its counterpoise; (vi) condensation of gas or moisture on the apparatus; (vii) variations in volume of the apparatus due to heating; (viii) inequalities in the arms of the balance; and (ix) the correction of the weight to vacuum standard. It is shown that the mean error arising from the above causes has the following values: (i) a temperature difference of 0·01° above the pans gives an error of 4/100 mg.; (ii) unsymmetrical pans, 1/100 mg.; (iii) a temperature difference of 0·1° above the balance arms, 2/100 mg.; (iv) weights with screwed heads, 1/100 mg.; (v) calibration of brass weights with platinum weights, 1/100 mg.; (vi) changes in the amounts of gas and moisture occluded on the weights and apparatus, 2/100 mg.; (vii) a difference of 0·1 c.c. between the volumes of the apparatus and the counterpoise, 2/100 mg.; (viii) variations of the gas or moisture absorbed on the surface of the apparatus, 2/100 mg.; (ix) change in volume due to heating, 2/100 mg.; and (x) error due to the reduction of the weight to vacuum standard by the ordinary method, 2/100 mg. per gram. It is thus obvious that a total error of 19/100 mg. is likely in a weighing. The author consequently deprecates the statement of weights to 1/100 mg., as is customary, unless these sources of error have been removed. It is shown that the construction of the balance arms of a stable bronze of low coefficient of expansion, weighing in a closed space of constant temperature, and finally with a balance which may be evacuated, the majority of the above-mentioned errors may be avoided. J. F. S.

Errors Affecting the Determination of Atomic Weights. II. Experimental Determination of the Vacuum Correction for the Weight of Powders. TH. RENARD and PH. A. GUYE (*J. Chim. phys.*, 1916, **14**, 55—82. Compare preceding abstract).—A number of experiments are described which have been carried out with the object of determining the dimensions of the correction which is to be applied to the weight of substance in the finely divided condition in order to reduce the weight to the vacuum standard. As a result of this work it is shown that the conditions under which the determination of the factors entering into the calculation of the vacuum correction is obtained do not admit of a greater accuracy than 1/100,000 of the weight of the substance taken, so that results given to 1/100 mg. on 5 grams of substance are illusory. Even when the correction factors are determined with the greatest accuracy, experiment shows that the calculated weight in a vacuum is sometimes a little less and sometimes a little larger than the true weight as experimentally determined, the order of the difference of the two values being ±1/100,000 of the weight of the substance. This difference is due to the inclusion of air in the powdered substance, and it is shown that the only way to get the vacuum weight of a finely divided substance is to weigh it actually in a vacuum. It is again shown that weights given to 1/100 mg. are from this cause also untrustworthy, and also that in most cases a weight accurate to 1/10 mg. is all that is necessary. J. F. S.

Errors Affecting the Determination of Atomic Weights. III. Various Methods in Use for Reducing Weight to the Vacuum Standard. PH. A. GUYE (*J. Chim. phys.*, 1916, **14**, 83—100. Compare preceding abstracts).—In the present paper the author reviews the various methods in use for the reduction of weight to the vacuum standard. It is shown that these methods furnish results which vary considerably in their degree of precision; thus the modern method (weighing of all substances in vacuum) yields atomic weights which on this account alone are liable to an error of 1/300,000; the method due to Stas yields figures accurate to 1/100,000, whilst that due to Marignac or Harvard contributes an error of 1/33,000. Since the actual agreement between different observers using different methods for the determination of the same atomic weight is 1/10,000, it follows that the whole of the methods for reduction to the vacuum standard are sufficiently precise. In view of the considerations of the present and preceding papers, it becomes obvious that all values of atomic weights with figures purporting to be accurate to 1/500,000 are illusory. J. F. S.

The Additivity of the Values of b and $\sqrt{a}$ of the Equation of State and the Fundamental Values of these Quantities for Different Elements in Connexion with the Periodic System. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1220—1235, and *J. Chim. phys.*, 1916, **14**, 3—24).—It is shown that the values of b are additive in character, and that constants may be derived for the different elements by means of which it

is possible to calculate the value of b for any substance containing these elements.

When the atomic constants for the elements of the carbon, nitrogen, oxygen, and fluorine groups of the periodic table are compared, it is found that in each group there is a regular increase in the value of $b \times 10^5$, which amounts to 55 units for each pair of adjacent homologues. In each horizontal series there is a regular decrease in $b \times 10^5$ equal to 15 units for each pair of adjacent elements. The atomic constants for hydrogen, carbon, nitrogen, and oxygen are apparently not invariable, but depend on the nature of the other atoms with which these elements are combined. The fundamental value for hydrogen is 48·5, but in many inorganic compounds it has the value $34 = 48{\cdot}5 \times \sqrt{2}/2$, and in organic compounds the value $14 = 48{\cdot}5 \times (1 - \sqrt{2}/2)$. In its inorganic compounds and in the aliphatic compounds carbon has the fundamental value $= 100$, but in the aromatic compounds the value for carbon is 75 (approximately equal to $100 \times \sqrt{2}/2$). The fundamental value for nitrogen $= 85$ is found only in the element; in all its compounds it has the smaller value $69 = 85 \times \sqrt{2}/2$. The value of 70 for oxygen is shown by most oxygen compounds, but a smaller value, $50 = 70 \times \sqrt{2}/2$, is obtained for oxygen doubly bound to carbon.

Additivity is also shown by the values of $\sqrt{a}$, where a is the attraction constant in the van der Waals's equation. The atomic constants obtained for the different elements belonging to the groups mentioned above are also found to exhibit simple relations when considered from the point of view of the periodic table. Approximately, the values of $\sqrt{a} \times 10^2$ for the elements in the first horizontal series are equal to 3. For the second, third, and fourth horizontal series the values of $\sqrt{a} \times 10^2$ are approximately 5, 7, and 9. Hydrogen and neon fall into line as members of the first horizontal series, whilst argon, krypton, and xenon fit quite satisfactorily into the second, third, and fourth series respectively. Since the value of $\sqrt{a} \times 10^2$ for helium is about 1 and for mercury 11, it would seem that $\sqrt{a} \times 10^2$ is exactly 2 units greater in each successive horizontal series.

The most important result which follows from the analysis of the available data is that the quadrivalent atoms carbon, germanium, and tin, as well as the tervalent atoms nitrogen and phosphorus, are of no account so far as the value of $\sqrt{a}$ is concerned when these atoms are symmetrically surrounded by other atoms or groups. This condition is attained when the quadrivalent or tervalent atoms are combined respectively with four or three univalent atoms or groups. In these circumstances, the influence of the central atom on the attractive forces between the molecules of which they form part is negligibly small.

H. M. D.

The Validity of Mathews's So called Valency Law. J. J. van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1235—1239).—A criticism of the views put forward by Mathews

(A., 1913, ii, 494, 674), according to which the attraction coefficient a may be expressed by the equation $a=C(M\times n)^{\frac{2}{3}}$, where M is the molecular weight of the substance concerned, n the total number of effective valencies, and C is a constant. It is shown that such a relation does not hold, and that it is quite inconsistent with the additivity of the atomic values of $\sqrt{a}$ (see preceding abstract).

H. M. D.

Considerations on Von Baeyer's Strain Theory. ADOLFO MELÓN (*Anal. Fis. Quim.*, 1916, **14**, 198—210).—A review of the strain theory from a mathematical point of view. A. J. W.

A New Form of Distilling Flask, together with a Note on Benzyl Benzoate. THE EARL OF BERKELEY (T., 1916, **109**, 520—523).—A vacuum-jacketed distilling flask is described which has proved to be useful in facilitating the distillation of substances of high boiling point.

The yield of benzyl benzoate obtained from benzaldehyde and benzyl alcohol by Claisen's method is considerably increased if the aldehyde and alcohol are dried and freshly distilled before use. Under these conditions the reaction also takes place more quickly.

H. M. D.

A New Condenser. SIGMUND FRÄNKEL (*Biochem. Zeitsch.*, 1916, **74**, 165—166).—A condenser of the ordinary Liebig type, but containing, instead of one condensing tube, seven narrow ones opening into single receptacles at each end. The apparatus is illustrated. S. B. S.

A Water-blower and a Laboratory Furnace. A. HUTIN (*Ann. Chim. anal.*, 1916, **21**, 94—95).—The mixture of water and air discharged from an ordinary water-pump is conducted through a tube to the bottom of a large glass bottle; the water collecting in the bottle is discharged through a second tube, also reaching to the bottom of the bottle, whilst the air collecting under pressure in the upper part of the bottle is led through a third tube to a blast burner. The bottle is closed with a rubber stopper, through which the tubes pass. The furnace described is constructed of hollowed-out fire-bricks arranged so as to form a cylindrical receptacle for a crucible. W. P. S.

A New Safety-valve. M. S. LOSANITCH (*Chem. News*, 1916, **113**, 218).—A safety-valve for preventing the back-flow of the water from water-pumps consists essentially of a cylindrical vessel provided with a nozzle towards the base for connecting to the pump, and with a vertical, narrow-bore tube internally, which is connected, likewise towards the base, with a second tube of somewhat more than the usual barometric height, fused through the walls of the above-mentioned cylinder and in communication at its upper end with the vessel being evacuated and with the manometer. The cylindrical vessel is filled with mercury to a point just below the junction of the internal tube with the long baro-

meter tube, so that under normal conditions there is a free passage between the pump through the upper end of the internal tube to the evacuated vessel. Should water suck back into the cylindrical vessel, however, its pressure causes the mercury to rise in the inner tube to beyond the junction, thereby cutting off completely the evacuated vessel from the cylindrical vessel and the pump.

G. F. M.

Inorganic Chemistry.

Iodide and Iodate Ion Content of Sea-water. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1916, **29**, i, 205—207. Compare this vol., ii, 184).—Iodine in organic combination was not found to be present in water from the Adriatic. The total iodine content of the water was approximately 0·05 mg. per litre. Near the surface, where the water was exposed to air and sunlight, the iodate-ion content predominated; at a greater depth the relation between the iodate and iodide changed, the proportion of the latter increasing. W. P. S.

The Citric Acid Solubility of the Phosphate in Thomas's Slag. PAUL KROLL (*Zeitsch. angew. Chem.*, 1916, **29**, i, 199—200). —The addition of sand in the converter raises the citric solubility of the phosphates in Thomas's slag on the average by about 1%. The soluble phosphate appears to have a tendency to remain constant for each particular type of slag, and to be more or less independent of the total phosphate present. This constant is about 18·5% for sand slag and 17·3% for normal slag. With lower phosphate content the insoluble phosphate is therefore less in amount than with a slag of high phosphate percentage.

G. F. M.

The Rare Gases in Natural Gases. CHARLES MOUREU and ADOLPHE LEPAPE (*Ann. Chim.*, 1915, [ix], **4**, 137—157; 1916, [ix], **5**, 5—51).—A résumé of work already published, full experimental details being given (compare A., 1906, ii, 685; 1907, ii, 22; 1908, ii, 277; 1909, ii, 363; 1910, ii, 136; 1911, ii, 392, 439, 602, 1087, 1134; 1912, ii, 47, 843; 1914, ii, 239, 357, 560).

W. G.

Complete Solubility Curve of Calcium Carbonate. JOHN JOHNSTON and E. D. WILLIAMSON (*J. Amer. Chem. Soc.*, 1916, **38**, 975—983).—In connexion with Johnston's paper on the solubility-product constant of calcium carbonate (A., 1915, ii, 769), a discussion is now given of the relation between the partial pressure of carbon dioxide in equilibrium with the solution and the total concentration of base in equilibrium with the solid phase, and a

graph has been constructed showing the concentration of calcium in the solution at equilibrium in the system $CaO-H_2O-CO_2$. The graph is composed of three curves, along which the stable solid phases are hydroxide, carbonate, and hydrogen carbonate respectively. The first extends only up to values of P, the partial pressure of carbon dioxide, of about 10^{-14} at 16°; the second, starting from the transition point, decreases to a minimum and then rises again, as the value of P increases, until it is about 15 atmospheres; beyond the second transition point hydrogen carbonate is the solid phase. Along the whole course of the graph the ions OH', CO_3'', and HCO_3' are all present in relative concentrations depending on P, and the solubility curve ascertained by experiment would thus have different forms according to which of the molecular species in solution was estimated. The transition pressure at which both hydroxide and carbonate are stable can be calculated from the solubilities of the hydroxide and carbonate or from their thermal dissociation pressures; the two methods give remarkably concordant results. E. G.

Molecular Transformations of Precipitates. A. VILLIERS (*Ann. Chim.*, 1916, [ix], **5**, 109—157).—A résumé of work already published, with certain modifications of detail (compare A., 1895, ii, 224, 227, 228, 247, 266, 267; Baubigny, A., 1882, 805, 928, 1031, 1032, 1172; 1888, 113; Thomsen, A., 1897, ii, 206). W. G.

The Melting Point of Tungsten. IRVING LANGMUIR (*Chem. Zentr.*, 1916, i, 205; from *Physical Review*, 1915, **6**, 138—157, and *J. Franklin Inst.*, 1915, **180**, 490—492).—The following values were found for the melting point of tungsten determined by three different methods, namely, tungsten wire in nitrogen, photometrically, and pyrometrically, and tungsten arc electrodes in nitrogen, pyrometrically: 3540°, 3332°, 3566°. The author considers $3540 \pm 30°$ as the best result. G. F. M.

Preparation of Pure Uranium and Other Metals. W. I. BARAGIOLA (*Chem. Zentr.*, 1916, i, 92; from *Schweiz. Apoth. Zeit.*, 1915, **53**, 477—478).—The author claims priority for the method of preparation of uranium described by Lely and Hamburger (A., 1914, ii, 569). He further mentions that pure copper which has been slowly distilled at least ten times in the vacuum of the mercury pump only has a pale rose colour. Similarly gold, after repeated distillation, loses somewhat its yellow colour. It has been suggested that pure copper is, like the other metals, of a whitish-grey colour. G. F. M.

Preparation of Colloidal Gold Solutions. J. TEMMINCK GROLL (*Chem. Weekblad*, 1916, **13**, 617—622).—An account of the preparation of colloidal gold solutions by reduction of auric chloride by hydrogen peroxide. A. J. W.

Mineralogical Chemistry.

Composition of Bornite. E. T. ALLEN (*Amer. J. Sci.*, 1916, [iv], **41**, 409—413).—The following analyses were made on material which was carefully examined for impurities by the metallographic method. They all conform closely with the formula Cu_5FeS_4 of Harrington (A., 1904, ii, 46), which had also been previously arrived at by Cleve in 1875. The materials analysed were from: I, Superior, Arizona; II, unknown locality; III, Costa Rica; IV, Bristol, Connecticut; V, Guildford Co., North Carolina; and VI, Messina, Transvaal. The formula proposed by Kraus and Goldsberry (A., 1914, ii, 570) is not accepted, the material analysed being impure.

	Cu.	Fe.	S.	Pb.	Ag.	Total.	D_4^{25}.
I.	62·99	11·23	25·58	0·10	nil	99·90	5·061
II.	63·19	11·31	25·44	nil	0·02	99·96	5·061
III.	63·08	11·22	25·54	nil	nil	99·84	5·037
IV.	63·26	—	—	—	—	—	5·064
V.	63·90	10·79	25·17	nil	nil	99·86	5·103 (D_{25}^{25})
VI.	63·24	11·12	25·54	—	—	99·90	5·079

L. J. S.

Synthesis of Obsidian and Pumice. WALTHER HEMPEL (*Zeitsch. angew. Chem.*, 1916, **29**, i, 173—175).—The synthesis of obsidian was realised by fusing a suitable silicate mixture in an atmosphere of water vapour at high pressures. Thus fusion of a mixture of felspar, quartz, iron-stone, and soda under a steam pressure of 85 atmospheres in an electrically heated oven enclosed in an autoclave (of which a detailed description is given) gave rise to a glass containing 0·65% of water which completely resembled obsidian in outward appearance and showed the same phenomenon of effervescence and evolution of water vapour on heating in the blow-pipe flame. If after fusion the pressure is suddenly released, the mass, on cooling, is porous, and resembles pumice-stone in all respects. It was shown, incidentally, that ferric silicates do not exist, and the ferric iron cannot therefore be regarded in these silicate mixtures as being in combination with silicic acid. The fusions in connexion with this work were conducted in vessels constructed of 0·02 mm. platinum foil folded in such a way as to fit tightly into magnesia crucibles. Such vessels made to fit into porcelain, quartz glass, or magnesia are recommended as substitutes for heavy, solid platinum vessels. G. F. M.

Mineral Gels. H. LEITMEIER (*Kolloid Zeitsch.*, 1916, **18**, 117—120).—A specimen of colloidal montmorillonite from Bulgaria was found on re-examination three years later to have undergone transformation into the crystalline form. Analysis gave:

Mg.	CaO.	Al_2O_3.	Fe_2O_3.	SiO_2.	H_2O.	Total.
2·28	1·26	19·74	4·14	50·14	22·61	100·17

corresponding fairly closely with $Al_2O_3,4SiO_2,6H_2O$. The crystallisation of the substance is in favour of the view that the substance is a chemical compound.

Blue and white specimens of a colloidal phosphate from Jakubeny, in the Bukowina, have proved to be colloidal forms corresponding with the crystalline minerals cœruleolactin and planerite ($3Al_2O_3,2P_2O_5,10H_2O$). The water content of the gel is variable and depends on the vapour pressure of the water in the surrounding atmosphere. The blue specimen is the purer variety, the blue colour of the gel being due to copper which has probably been adsorbed. H. M. D.

Action of Water Vapour at High Temperature on Volcanic Rocks. ALBERT BRUN (*Arch. Sci. phys. nat.*, 1916, [iv], **41**, 401—418).—Estimations were made of the gases (HCl, CO_2, CO, H_2, N_2, SO_2) which are evolved in considerable amounts when various volcanic rocks are heated at temperatures of about 1000° in the presence of water vapour. Under similar conditions olivine gives off CO_2, CO, N_2, and H_2, the former two being derived from enclosed bituminous matter. The results are taken to support the author's theory of volcanic action (A., 1907, ii, 33).

L. J. S.

Analytical Chemistry.

The Centrifugal Machine in the Chemical Laboratory. H. J. Hamburger (*Chem. Weekblad*, 1916, **13**, 636—643).—A plea for the use of the centrifuge for washing precipitates, and in quantitative analysis for determining the volume of precipitates.

A. J. W.

Estimations by means of Critical Mixture Points. W. J. de Mooy (*Chem. Weekblad*, 1916, **13**, 608—616).—A lecture delivered before the Leyden Chemical Society. A. J. W.

The Estimation of the Hydrion Concentration of very Small Quantities of Liquids. R. J. Wagner (*Biochem. Zeitsch.*, 1916, **74**, 239—242).—The method is devised for the measurement of the hydrion concentration of a few millimetres of fluid. Lacmosol, prepared by Hottinger's method, is dissolved in thirty times its weight of 6% collodium containing a little alcohol. This gel is spread on an object-glass and placed for some minutes over potassium hydroxide in a desiccator. Ten c.mm. of the liquid under investigation are added, and the glass is then replaced in the desiccator. A scale of colour is prepared on another plate in a similar manner with liquids of known hydrion concentration

made from citric acid and a base. The final estimation of the p_H is made colorimetrically. The limitations and difficulties of the method are indicated by the author. It is available between the limits $p_H = 4 \cdot 2$ and 6·0. S. B. S.

Estimation of Hydrogen Peroxide. JOSEPH VON BERTALAN (*Chem. Zeit.*, 1916, **40**, 373—374).—The inexactitudes involved in the titration of hydrogen peroxide in presence of oxidisable organic matter by the usual permanganate or iodometric methods are obviated by the use of stannous chloride, which reacts according to the equation $SnCl_2 + 2HCl + H_2O_2 = SnCl_4 + 2H_2O$. The estimation may be made by either a direct or back titration; in the former case a 1% solution of methylene-blue serves as indicator, and in the latter the excess of stannous chloride is titrated back with iodine. In order to avoid oxidation of the stannous solution, the peroxide solution is acidified with sulphuric acid and a little solid potassium hydrogen carbonate is added, and the stannous chloride is then run in during the ensuing effervescence. When carefully preserved in an oxygen-free atmosphere the titration value of stannous chloride solution does not appreciably alter, but it is advisable to control the solution by a blank titration with permanganate before use. G. F. M.

Transformations during the Ignition of Foodstuffs containing Sodium Chloride. A Reaction between Carbon and Sodium Chloride. J. D. FILIPPO and W. ADRIANI (*Chem. Weekblad.*, 1916, **13**, 405—410).—The loss of chlorine attendant on the ignition of foodstuffs containing sodium chloride is not due to the presence of acid phosphates, but to reduction of the chloride by carbon or its compounds. A. J. W.

A New Method of Estimating Fluorine. F. PISANI (*Compt. rend.*, 1916, **162**, 791—793).—Fluorine in solution as an alkali fluoride is readily precipitated in the cold as thorium fluoride, $ThF_4,4H_2O$, by the addition of thorium nitrate to the solution slightly acidified by acetic acid or, better, nitric acid. The precipitate is gelatinous, voluminous, and heavy. It readily settles and can be easily washed by decantation. For the final washings on the filter-paper, it may be necessary to employ suction. The precipitate is dried and ignited, yielding thorium oxide, which is weighed. Care must be taken to avoid using an excess of thorium nitrate, as the precipitate is slightly soluble in this solution. The reaction is sufficiently sensitive to permit of the detection of 0·01% of fluorine in a solution. Insoluble fluorides, fluorapatites, and such substances are subjected to the usual preliminary treatment to obtain the fluorine in solution, and any phosphate in solution must be precipitated in the usual way before adding the thorium nitrate. Silicofluorides in solution may be precipitated directly with thorium nitrate and the precipitate ignited to thorium oxide. Soluble tantalofluorides are first boiled with sodium carbonate and the tantalic acid filtered off, and then the fluorine is precipitated as above. W. G.

Examination and Valuation of "Nitrolime." PAUL LIECHTI and ERNST TRUNIGER (*Chem. Zeit.*, 1916, **40**, 365—366).—The extraction of "nitrolime" with water, as recommended by Caro (A., 1911, i, 119), preliminary to the estimation of cyanamide gives low results, owing possibly to the presence of basic calcium cyanamide compounds, which are but sparingly soluble in water. Extraction with dilute nitric acid in quantity sufficient to neutralise all the lime present is recommended, and after two hours' shaking the filtered extract is rendered alkaline with ammonia and precipitated with silver nitrate in the usual manner. Stress is laid on the necessity of discriminating between cyanamide-nitrogen and dicyanodiamide-nitrogen in analyses of this substance, as if stored in a damp place it may lose almost its entire cyanamide content, owing to conversion into the supposedly worthless or even harmful dicyanodiamide. G. F. M.

Admissibility of Ammonium Magnesium Phosphate as a Form in which to Weigh Phosphoric Acid. WALTER JONES (*J. Biol. Chem.*, 1916, **25**, 87—91).—When precipitated crystalline ammonium magnesium phosphate is collected on a weighed filter-paper and allowed to dry in the air, its weight in a few hours becomes constant, and its composition is exactly expressed by the formula $MgNH_4PO_4,6H_2O$. These results indicate that in the quantitative estimation of phosphoric acid the conversion of magnesium ammonium phosphate into magnesium pyrophosphate is a superfluous operation. H. W. B.

The Estimation of Carbon by the Eggertz Method. H. LE CHATELIER and F. BOGITCH (*Compt. rend.*, 1916, **162**, 709—714; 731—735).—The first paper is a critical study of the errors likely to occur with variations in conditions, using the Eggertz method for the estimation of carbon in steel.

The comparison solutions should be kept in the dark and made fresh once a week, as they slowly change in sunlight and ultimately lose all their colour. Solutions of caramel, which have been suggested as comparison liquids, are equally sensitive to light. If the comparison is made at temperatures above 50°, the results will not be correct, owing to increase in the coloration due to hydrolysis of the ferric salts, the coloration increasing with the temperature. In preparing the solution from the steel, the longer it is heated the less is the colour obtained. With the same carbon content in the steel and the same time of heating, the coloration decreases as the concentration of the acid increases. The presence of hydrochloric acid in the nitric acid causes a diminution in the colour produced, but sulphuric acid has little or no effect.

The following are the most satisfactory conditions for the estimation. To 1 gram of steel turnings 20 c.c. of nitric acid (D 1·16) are added, and the liquid brought to the boil in one minute. After one minute's boiling, 30 c.c. of boiling acid (D 1·33) are added, and the boiling is continued for three minutes. The whole is then rapidly cooled in water, and the colorimetric

comparison is made either with a type of known composition or with a freshly prepared caramel solution corresponding with a given type.

The second paper contains an examination of the influence of variations in the nature of the steel, the nature and amount of foreign substances present, and the structure of the metal due to different thermal treatment on the results obtained for carbon content by the Eggertz method. Contrary to the results of Deshayes, the authors find that, using the rapid method with boiling solvents (*loc. cit.*), the results obtained for the carbon content of steels, over as wide a range as C=0·9—1·20%, all come within the limits of experimental error. Further, the presence of manganese lowers the apparent carbon content; but this influence is small where the manganese does not exceed 1%, and if a steel containing 0·5% manganese is used as a type the error is largely eliminated. Nickel also lowers the apparent carbon content, and its effect is much greater than that of manganese. Steels containing more than 3% of nickel give green solutions which are difficult to compare against the standard. Silicon, provided it is below 1%, does not interfere with the estimation. Variations in the velocity of cooling the steel considerably modify the colour due to the carbon, and also the hardness, even with velocities too small to produce true tempering and the formation of martensite. The fineness of the cementite contained in the perlite also modifies both the solubility of the carbon and the hardness of the metal. This influence of the velocity of cooling is much more marked the richer the steel is in manganese, the coloration being sometimes reduced by as much as one-third. In order therefore to obtain satisfactory results with the Eggertz method, it is essential to use samples of steel cooled slowly and to use as a type for comparison a steel having practically the same manganese content as the one under examination. W. G.

Frequent Sources of Error in the Analysis of Generator Gas FRITZ HOFFMANN (*Chem. Zeit.*, 1916, **40**, 412—413).—The difficulty with which carbon monoxide is absorbed by ammoniacal cuprous chloride solution introduces an error in the estimation of this gas, and also of the hydrogen and methane in generator gas. It is recommended that these three gases should be estimated by the combustion method and that both the contraction in volume and the quantity of oxygen used for the combustion should be determined. W. P. S.

Estimation of Carbon Dioxide as Barium Carbonate Applied to the Marr Method for Estimating Carbonates in Soils. C. J. SCHOLLENBERGER (*J. Ind. Eng. Chem.*, 1916, **8**, 427—428).—Trustworthy results may be obtained by absorbing the carbon dioxide evolved from the soil according to the conditions prescribed in the Marr method (A., 1909, ii, 938) in barium hydroxide solution, and titrating the barium carbonate formed as described by Cain (A., 1914, ii, 577) W. P. S.

Estimation of Carbonic Acid, Combined and Free, in Solution, Particularly in Natural Waters. JOHN JOHNSTON (*J. Amer. Chem. Soc.*, 1916, **38**, 947—975).—Although a great deal of work has been done in connexion with the estimation of carbonic acid in solutions, the subject has not received much attention from the theoretical side. In the present paper, therefore, the methods of estimating carbonic acid and carbonates are discussed from the following point of view. The several molecular species concerned can co-exist only in definite proportions determined by the known equilibrium constants, since within any solution containing carbonate there is a readily attained equilibrium between the carbonate ion, CO_3'', the hydrogen carbonate ion, HCO_3', and the carbonic acid, H_2CO_3, and, in turn, between the carbonic acid and the partial pressure of carbon dioxide above the solution. It is shown that many of the most commonly used titration methods for estimating combined and free carbonic acid in solution do not yield definite results. In principle, the only absolutely trustworthy methods are those in which the total base, equivalent to the combined carbonic acid, and the total carbonic acid, free and combined, are estimated; the conditions are pointed out under which such methods yield accurate results in practice. These two estimations are generally sufficient, since with a knowledge of these quantities and the equilibrium constants the concentration can be calculated of carbonate and hydrogen carbonate, and also that of the hydrogen ion, which is a measure of the degree of acidity or alkalinity of the water. E. G.

Estimation of Silica. VICTOR LENHER and EMIL TRUOG (*J. Amer. Chem. Soc.*, 1916, **38**, 1050—1063).—A study has been made of the various sources of error in silica estimations and the best means of avoiding them. The results have led to the adoption of the following method of estimation.

A sample of the silicate (0·5—1·0 gram) is mixed with 5 grams of sodium carbonate and fused in a platinum crucible. When cold, the product is treated with 60 c.c. of hydrochloric acid (D 1·07) and heated on the water-bath until the residue begins to powder or crumble. The residue is treated with 15 c.c. of hydrochloric acid (D 1·1), and the vessel is covered and heated on the water-bath for ten minutes. Water (10 c.c.) is added, the mixture is filtered immediately, and the silica washed with a hot solution of 5 c.c. of hydrochloric acid (D 1·2) to 95 c.c. of water. The filtrate is evaporated to dryness, and the residue heated at 110° for two hours and then treated with 8 c.c. of hydrochloric acid (D 1·1); the vessel is covered and heated on the water-bath for five to ten minutes, and the product is diluted to about 50 c.c. and immediately filtered without suction. The residue is washed with cold water containing 1 c.c. of hydrochloric acid to 99 c.c. of water. The paper and silica after being dehydrated at 110° are placed in a platinum crucible, and the paper is burned. The silica from the first dehydration is then added to the crucible, and the silica is ignited until the weight is constant. The silica is

then estimated in the usual way by volatilisation with hydrofluoric acid after the addition of a few drops of sulphuric acid.

It is important that in dehydrating the silica the temperature should not be allowed to rise above 110°. Dehydrated silica is appreciably soluble in hydrochloric acid, but when dilute acid is used the error is almost negligible. Dehydrated silica is slightly soluble also in solutions of sodium chloride. E. G.

Detection of Silver Chloride on Photographic Plates, etc. E. VALENTA (*Chem. Zeit.*, 1916, **40**, 398).—When silver chloride is treated with potassium ferrocyanide, reaction takes place according to the equation: $K_4Fe(CN)_6 + 4AgCl = Ag_4Fe(CN)_6 + 4KCl$, whilst silver bromide and silver iodide do not react with the ferrocyanide. Silver ferrocyanide is a white, insoluble compound which changes to silver ferricyanide, an orange-red compound, on the addition of nitric acid. To detect the presence of silver chloride on photographic plates, films, etc., the latter are washed to remove soluble silver salts, then immersed for a few minutes in 5% potassium ferrocyanide solution, again washed, dried between filter-paper, and a drop of concentrated nitric acid is placed on the sensitive surface of the plate. An orange-red coloration appears at once if silver chloride is present. If, after the plate has been treated with ferrocyanide and washed, a drop of potassium bromide solution containing ferric chloride is placed on the surface, a blue coloration is obtained in the presence of silver ferrocyanide; this is due to the silver ferrocyanide reacting with the bromide, with the formation of silver bromide and potassium ferrocyanide, the latter then giving a blue coloration with the ferric chloride. Freshly precipitated silver bromide is reduced slightly when treated with ferrocyanide in bright light; silver ferrocyanide is formed, and a reaction may be obtained indicating the presence of chloride. Light should therefore be excluded in making the test. W. P. S.

Density of Aqueous Solutions of Copper Sulphate and Sulphuric Acid. H. D. HOLLER and E. L. PEFFER (*J. Amer. Chem. Soc.*, 1916, **38**, 1021—1029).—In connexion with the use of acid copper sulphate solutions for electro-deposition, and especially for electrotyping, a simple method is desirable for determining and adjusting their composition. Since the solutions usually employed contain only copper sulphate and sulphuric acid, their composition can be calculated from a knowledge of the amount of acid present and the density at a given temperature. The density can be readily determined by means of a hydrometer, and the acidity can be estimated by titration with standard alkali hydroxide, methyl-orange being used as indicator (Wogrinz, A., 1913, ii, 788).

A table has been constructed showing the density of solutions containing from 0 to 20% of each of the constituents at 25° and 40°; the data are also represented by means of curves. It is found that within the range mentioned the density of solutions containing copper sulphate and sulphuric acid is approximately

a linear function of the concentration, and that the density of solutions of equal concentration (that is, containing the same number of grams per litre) of copper sulphate ($CuSO_4,5H_2O$) and of sulphuric acid is nearly identical. The density of solutions containing appreciable amounts of each constituent depends therefore principally on the total concentration of the two solutes, and is almost independent of their proportions. It follows that the composition of acid copper sulphate solutions can be ascertained by determinations of the density and acidity, since on deducting the concentration of the sulphuric acid from the total concentration corresponding with the observed density the concentration of the copper sulphate is obtained. E. G.

Separation of Metals of the Tin Group. J. M. WELCH and H. C. P. WEBER (*J. Amer. Chem. Soc.*, 1916, **38**, 1011—1016).—The usual methods for the qualitative separation of arsenic, antimony, and tin are not altogether satisfactory for elementary students, and a new method has therefore been devised which can be carried out under wider conditions and is more rapid and more easily manipulated.

The precipitated sulphides from the ammonium sulphide separation, after being drained by suction or between filter-papers, are treated with 10 c.c. of hydrochloric acid (D 1·20) and heated for ten minutes on the steam-bath. Arsenic sulphide remains, and is removed by filtration. The filtrate is diluted to 70 c.c. and saturated with hydrogen sulphide. If the hydrogen sulphide is introduced while the solution is hot, red antimony sulphide is first precipitated, and subsequently a brown precipitate (possibly a thioantimonite of tin) is formed which is characteristic of a mixture of tin and antimony; the depth of colour of this precipitate gives an indication of the relative proportions of the two constituents. The solution and precipitate are now heated to drive off the excess of hydrogen sulphide. Five c.c. of hydrogen peroxide (3%) are added, and the solution is heated until the precipitate has redissolved. Oxalic acid (5—10 grams) is added and hydrogen sulphide passed into the hot solution, which is allowed to cool while being saturated. Antimony sulphide separates as a bright red precipitate, and is removed by filtration. The filtrate is boiled with 1—2 grams of granulated lead for two to three minutes, and afterwards cooled and filtered into a solution of mercuric chloride, when the presence of tin is revealed by the precipitation of mercurous chloride. E. G.

The Destruction of the Organic Substance for the Detection of Mineral Poisons. J. VINTILESCO (*Chem. Zentr.*, 1916, i, 234; from *Bul. Soc. Ştiinte Bucureşci*, 1915, **17**, 99—110).—The author criticises the various methods for the destruction of organic material in forensic analysis, and recommends the potassium chlorate method, operating in the following way: 200 grams of the finely divided material are heated with 20 grams of potassium chlorate on the water-bath until the evolution of ammonia ceases; 35—40 c.c. of hydrochloric acid (D 1·19)

are then added in 5 c.c. portions at five to ten minutes' intervals, the heating being continued until the evolution of chlorine has ceased. The temperature rises to 90—95°, and in half to three-quarters of an hour sinks again to about 85°, at which point 10—20 c.c. of pure nitric acid (D 1·37) are added, the dish being allowed to remain on the water-bath in order to expel the greater part of the acid. Only about 10% of the original organic matter, mostly fat, remains undestroyed by this treatment, and the yellow reaction product serves for the subsequent toxicological examination. G. F. M.

Comparison of the Permanganate Methods for the Estimation of Required Oxygen [in Waters]. JOHN H. SACHS (*J. Ind. Eng. Chem.*, 1916, **8**, 404—406).—Investigation of the oxidation of various organic substances in acid aqueous solution by permanganate showed that temperature, time of contact, excess of permanganate, etc., have a considerable influence on the amount of oxygen absorbed. At temperatures above 85°, the more oxygen is absorbed the greater the excess of permanganate added. Comparative results can be obtained only when estimations are carried out under identical conditions. Oxidation with permanganate in alkaline solution yields untrustworthy results. W. P. S.

Estimation of Small Quantities of Dextrose in Urine. S. NAGASAKI (*Zeitsch. physiol. Chem.*, 1915, **95**, 61—77).—The method consists in estimating the reducing power of the urine by Benedict's process (A., 1911, ii, 340) before and after fermentation with *Torula monosa*, a yeast which attacks only monoses, including dextrose. If after treatment with the yeast the urine is boiled for seven minutes with 2% citric acid, a further quantity of monose is produced which apparently is derived from the biose, *iso*maltose, present in normal urine. The percentage of dextrose in normal urine varies from 0·033 to 0·002 (average 0·012) and of *iso*maltose from 0·023 to 0·003 (average 0·012).

By means of this method an increase in the urinary dextrose may in some cases be detected after the ingestion of as little as 25 grams of dextrose, especially when the diluting effect of the diuresis is taken into account. The *iso*maltose is also increased, but not to a corresponding extent. H. W. B.

The Estimation of Reducing Sugars by Kendall's Solution and the Construction of a Table Indicating the Reducing Power of Lævulose. EDITH GERTRUDE WILSON and WILLIAM RINGROSE GELSTON ATKINS (*Biochem. J.*, 1916, **10**, 137—141).—The contents of this paper are sufficiently indicated in the title. S. B. S.

Estimation of Raffinose in the Presence of Sucrose. H. PELLET (*Ann. Chim. anal.*, 1916, **21**, 89—91).—Attention is drawn to a method proposed by Hudson and Harding (A., 1914, i, 1147; 1915, ii, 803). If the method is used for the estimation of raffinose

in such substances as molasses, etc., the sample must be treated previously with basic lead acetate, the excess of lead removed, and the solution then saturated with calcium carbonate in order to neutralise any mineral acid which may be present and to precipitate remaining traces of lead. W. P. S.

The Disturbing Influence of Certain Physiologically Important Substances on the Colour Reaction between Iodine and Starch. A. CLEMENTI (*Chem. Zentr.*, 1916, i, 179; from *Arch. Farm. sperim.*, 1915, **20**, 258—268).—The blue iodine-starch coloration is destroyed by furfuraldehyde. The velocity of decolorisation is directly proportional to the amount of furfuraldehyde and inversely proportional to that of iodine, and with a large quantity of iodine or a very small quantity of furfuraldehyde decolorisation is not produced. Certain proteins (albumins, globulins, plant proteins, albuminoids, and phosphoprodeins) also cause a more or less rapid decolorisation. Glycine, alanine, leucine, and asparagine do not possess this property, but tyrosine and adrenaline probably do. G. F. M.

Estimation of Soluble Nitrocellulose in Guncotton. H. C. MALLINSON (*J. Ind. Eng. Chem.*, 1916, **8**, 401—402).—Five grams of the sample are treated with 200 c.c. of ether-alcohol mixture in a stoppered cylinder. After settling, 50 c.c. of the solution are transferred to a porcelain basin and 500 c.c. of water at 80° are added slowly. If the nitrocellulose thus precipitated forms a compact disk, this is removed to a piece of filter-paper, pressed with another piece of filter-paper, then dried for twenty-nine minutes at 71°, and weighed. In cases where the addition of water precipitates the nitrocellulose in a flocculent or disintegrated form, the latter must be collected on a filter, washed with alcohol, dried, and weighed. W. P. S.

Qualitative Tests for Gum Arabic and its Quantitative Estimation. C. E. WATERS and J. B. TUTTLE (*J. Ind. Eng. Chem.*, 1916, **8**, 413—416).—Basic lead acetate gives the most characteristic reaction for the purpose of distinguishing gum arabic from other gums and dextrins. Mixtures of copper sulphate and sodium hydroxide, and of ferric chloride and alcohol, are of value as confirmatory tests. An ammoniacal copper acetate solution containing 50% of alcohol is the best precipitant for gum arabic; the precipitate formed should be washed with alcohol, dried at 105°, weighed, then ignited, and the residue of copper oxide deducted from the weight of the precipitate to obtain the amount of the gum. W. P. S.

Reactions of Lignone. C. F. CROSS and E. J. BEVAN (*J. Soc. Dyers*, 1916, **32**, 135—141).—See this vol., i, 467.

Estimation of Tartaric Acid. B. G. HARTMANN, J. R. EOFF, and M. J. INGLE (*J. Ind. Eng. Chem.*, 1916, **8**, 422—425).—The

addition of potassium acetate in the estimation of tartaric acid as potassium hydrogen tartrate does not entirely prevent a reversible reaction between tartaric acid and potassium chloride, and it also has a solvent action on the hydrogen tartrate. The authors recommend that, in the estimation of tartaric acid in wine, the latter should be neutralised with sodium hydroxide, a quantity of tartaric acid equivalent to the amount of alkali used then added, and glacial acetic acid next introduced, followed by the usual quantities of potassium chloride and alcohol. The mixture must be stirred until a precipitate is formed. After the precipitated potassium tartrate has been collected and titrated, the quantity of added tartaric acid is deducted from the result. The tartaric acid may also be added in the form of Rochelle salt. In dealing with synthetic solutions containing tartaric acid, phosphoric acid, and alcohol, it was found that esterification occurred gradually, and that a preliminary saponification was necessary in order to obtain the whole of the tartaric acid. W. P. S.

Separation of Autogenous and Added Hydrocyanic Acid from Certain Plant Tissues and its Disappearance during Maceration. CARL L. ALSBERG and OTIS F. BLACK (*J. Biol. Chem.*, 1916, **25**, 133—140).—In the estimation of hydrocyanic acid in cyanogenetic plant tissues, it is advisable to continue the distillation with dilute sulphuric acid for at least four hours, because the liberation of the hydrocyanic acid from some plants only takes place slowly.

During the maceration of plant tissues containing hydrocyanic acid, a certain amount of the hydrocyanic acid present or of cyanide that may be added is so altered that it is not recoverable by distillation with sulphuric acid. This change is not due to the action of enzymes or to the presence of dextrose. Maceration should therefore be avoided as much as possible in the preparation of plant tissues for the estimation of hydrocyanic acid.

H. W. B.

Colorimetric Estimation of Uric Acid in the Blood. H. F. HÖST (*Zeitsch. physiol. Chem.*, 1915, **95**, 88—99).—Several improvements in Folin and Denis's method (A., 1913, ii, 162) are recommended. Operating on only 5 c.c. of blood, it is found that after the addition of 35 c.c. of water, 5 drops of 2% acetic acid, and 1 c.c. of neutral formaldehyde 13% solution, the protein is completely precipitated on boiling, and the filtrate is absolutely colourless. The liberation of the uric acid from the silver urate subsequently produced is found to be effected more readily by boiling in the centrifugal tube with hydrogen sulphide and acetic acid than with hydrochloric acid. H. W. B.

New Method for the Analysis of Rancid Fats. GIOVANNI ISSOGLIO (*Atti R. Accad. Sci. Torino*, 1916, **51**, 582—605).—The number of mg. of oxygen necessary to oxidise the organic compounds removed by the distillation of 100 grams of a fat in a current

of steam is termed the "oxidisability number." Between 20 and 25 grams of the fat, exactly weighed, and about 100 c.c. of water are introduced into a long-necked distilling flask and distilled in a current of steam, 100 c.c. of distillate being collected in ten minutes. Ten c.c. of the mixed distillate, 50 c.c. of distilled water, 10 c.c. of 20% sulphuric acid, and 50 c.c. of 0·01*N*-potassium permanganate solution are then heated to boiling and kept boiling for five minutes in a flask fitted with a ground-in condenser. After the flask has cooled somewhat, 50 c.c. of 0·01*N*-oxalic acid are introduced, and the contents then titrated with 0·01*N*-permanganate. If X c.c. of the latter are used, and the volume required for a blank test in which the fat is replaced by 10 c.c. of distilled water is x, the oxidisability number will be given by the expression $80(X-x)/P$, P being the weight of fat taken. For normal, fresh fats used as foods the oxidisability number varies from 3 to 10, rancid fats giving higher values; a number exceeding 15 justifies the statement that the fat has undergone alteration. T. H. P.

Comparison and Identification of Various Types of Smoking Opium. FRANK D. SIMONS (*J. Ind. Eng. Chem.*, 1916, **8**, 345—351).—Opium used for smoking, and prepared by simple extraction of crude opium with water and evaporation of the filtered extract until the residue contains from 15% to 20% of water, may be distinguished from opium extract intended for medicinal purposes by reason of its water content; medicinal opium is usually much drier, but in some cases the line of demarcation is very slight. The morphine content may also vary considerably from the 20% basis required by the U.S. Pharmacopœia. Another class of opium intended for smoking is prepared by heating, kneading, and partly roasting crude opium before it is extracted, filtered, and evaporated; this product is practically free from codeine, papaverine, and narceine, and the amount of thebaine is diminished considerably. The ratio of morphine to total alkaloid lies between 1 : 1·11 and 1 : 1·5. Products containing pipe-scrapings also show an abnormal alkaloid ratio; the quantity of ash often exceeds 8%, and there is present a characteristic odour. The usual physical, chemical, and microscopical tests will distinguish the smoking opiums prepared by mixing opium with foreign substances. W. P. S.

Proteins. III. Estimation of the Monoamino-dicarboxylic Acids. A. C. ANDERSEN and REGITZE ROED-MÜLLER (*Biochem. Zeitsch.*, 1916, **73**, 326—339).—The filtrate from the phosphotungstic acid precipitate of the hydrolysis products is neutralised by sodium hydroxide in the same way as is usual for formalin titrations. The monoaminomonocarboxylic acids are then in the free state, and only the dicarboxylic acids are in the form of sodium salts. If, then, the solution is evaporated to dryness and charred, the sodium carbonate of the ash will be equivalent to the amount of the dicarboxylic acids present; this can be estimated in the usual manner. If nitrogen-free acids are also present (and this

is not usual), or in the case of proteins which yield a large amount of glucosamine, the method cannot be employed. S. B. S.

Estimation of Albumin in Urine. René Dhommée (*J. Pharm. Chim.*, 1916, [vii], **13**, 241—249).—Ten c.c. of the urine, filtered previously if turbid, are placed in a tube, the lower portion of which is tapered and graduated, and 5 c.c. of precipitant are added. The latter consists of a mixture of glacial acetic acid 100 grams, trichloroacetic acid 10 grams, picric acid 10 grams, and water 1000 c.c. The tube is closed with a cork, its contents mixed, and, after ten minutes, submitted to centrifugal action for three minutes. The volume of the precipitate is then noted. The volume is not proportional to the amount of albumin present; for instance, 1 c.c. of precipitate corresponds with 1·5 grams of albumin per litre of urine, whilst 3 c.c. corresponds with 8 grams per litre. If desired, the tube may be so graduated that the readings give the weight of albumin per litre directly. W. P. S.

Comparison of Methods for the Estimation of Casein in Milk. C. B. Hersey (*J. Ind. Eng. Chem.*, 1916, **8**, 335—336).—The Hart method gave results which agreed closely with those obtained by the Kjeldahl-Gunning method; in estimations of casein in 143 samples of milk, 75% of the results by the two methods agreed within 0·1%. The van Slyke volumetric method was found to be less trustworthy, only 36% of the results agreeing within 0·1% with those obtained by the other methods.

W. P. S.

Modification of Wohlgemuth's Method of Estimating the Activity of Amylase in Presence of Alkaloids. J. Bodnár (*Chem. Zentr.*, 1916, i, 37—38; from *Fermentforsch.*, 1915, **1**, 347—350).—The action of alkaloids and similar substances on amylase is utilised. After the action has taken place, the solution is made alkaline with sodium hydroxide and the alkaloid extracted; it is then neutralised with hydrochloric acid, and the estimation continued by Wohlgemuth's method.

Morphine and strychnine have no effect on the amylase of pea seeds, or, according to Goebel, on Taka diastase. It is therefore considered probable that the diastases of peas and of *Aspergillus oryzae* are identical. N. H. J. M.

New Way of Carrying Out the Peroxydase Reaction in Milk. W. Grimmer (*Milchw. Zentr.*, 1915, **44**, 246—247).—The use of guaiacol and ethyl hydroperoxide is recommended for the detection of peroxydase in milk, since dilute solutions of these two substances remain stable for several years; they possess, therefore, a distinct advantage over guaiacum tincture and hydrogen peroxide solution. The test is carried out by mixing a few c.c. of milk with two drops of guaiacol solution (1 gram of guaiacol dissolved in 10 c.c. of alcohol and diluted with water to 100 c.c.) and adding two drops of a 0·1% ethyl hydroperoxide solution. Unheated milk yields a brick-red coloration, whilst boiled milk

remains colourless. The ethyl hydroperoxide may be prepared by the method described by Baeyer and Villinger (A., 1901, i, 308).

W. P. S.

Analysis of Rhamnus Barks. O. TUNMANN (*Chem. Zentr.*, 1915, ii, 1219—1220; from *Apoth. Zeit.*, 1915, **30**, 493—496. Compare this vol., ii, 60).—A weighed quantity of 1·6 grams of the dry, powdered bark is boiled with 100 grams of sodium hydroxide solution (a 4% solution in the case of *Rhamnus frangulus* and *R. carniolicus*, and a 3% solution with *R. purshianus* and *R. catharticus*), shaken for ten minutes, allowed to settle, and the liquid portion filtered. The insoluble portion is again shaken for ten minutes with 60 grams of the sodium hydroxide solution, filtered, and washed with sodium hydroxide solution and water. The united filtrates and washings are acidified, shaken for thirty minutes with 160 grams of chloroform, and, after two hours, the chloroform layer is separated, filtered, and 120 grams of it are shaken with 120 grams of the sodium hydroxide solution. The alkaline solution is filtered, 100 c.c. of the filtrate are acidified with hydrochloric acid, and, after about fifteen hours, the precipitate formed is collected on a weighed filter, washed with 1% hydrochloric acid, dried at 60°, and weighed. The following quantities of anthraquinones were obtained from the various barks: *R. frangulus*, 3·8%; *R. carniolicus*, 4·1%; *R. purshianus*, 1·8%; *R. catharticus*, 0·8% to 2·7%. In the case of *R. catharticus*, the quantity of anthraquinones appears to increase with the age of the bark. The precipitates obtained are not quite free from ash. If *frangula* bark is shaken with cold sodium hydroxide solution, the foam produced is coloured red; *sagrada* bark yields a light, brown-coloured foam under similar conditions. W. P. S.

New Apparatus for the Estimation of Soil Carbonates and New Methods for the Estimation of Soil Acidity. E. TRUOG (*J. Ind. Eng. Chem.*, 1916, **8**, 341—345).—The soil is decomposed by hydrochloric acid in a tapped funnel, the top of which is connected with a wash-bottle containing silver sulphate; the stem of the funnel is bent upwards and then outwards. Air free from carbon dioxide is drawn through the apparatus, and the liberated carbon dioxide is absorbed in barium hydroxide solution contained in an absorption tower, described previously by the author (this vol., ii, 113).

The method for the estimation of active soil acidity consists in treating the soil with an excess of barium hydroxide solution for one minute, passing a current of carbon dioxide into the mixture, then evaporating the latter, and estimating the excess of carbonate. Total soil acidity is estimated similarly, but the mixture of soil and barium hydroxide is boiled for thirty minutes; the latent soil acidity is the difference between the total acidity and the active acidity. A method is proposed for determining the avidity of active soil acids; the soil is shaken for two minutes with potassium acetate solution, filtered, and the acidity of the filtrate titrated. W. P. S.

General and Physical Chemistry.

The High-frequency Spectra (L Series) of the Elements Tantalum to Uranium. MANNE SIEGBAHN and EINAR FRIMAN (*Phil. Mag.*, 1916, [vi], **32**, 39—49).—An account of experiments the results of which have been previously published (compare this vol., ii, 277, 362). H. M. D.

Relationships in Band Spectra. L. KILCHLING (*Zeitsch. wiss. Photochem.*, 1916, **15**, 293—313, 317—360).—A theoretical paper, in which the author discusses the relations between the frequencies of the lines which collectively form the bands and also the relations which are exhibited by the edges of the several bands which belong to one and the same group. It is shown that, in both cases, the frequency relations can be represented by a series formula of the type $\nu = a \pm bm^2 \mp cm^4 \pm dm^6 \mp em^8 \pm \ldots$, in which $a, b, c, d, e \ldots$ are positive constants, and m is a number which expresses the order of the line or band of frequency ν. By application of this formula to the line series of the cyanogen band $\lambda_0 = 3883 \cdot 55$ and of the green carbon band $\lambda_0 = 5634 \cdot 24$, and also to the band series of the absorption spectrum of iodine, it is shown that the three constant formula, $\nu = a \pm bm^2 \mp cm^4$ affords a satisfactory agreement with the experimental measurements.

By the assumption of Rutherford's model atom, a formula has been derived for the frequency relations which is quite consistent with the above series formula. The theoretical analysis involved in this process leads to the conclusion that the line series constituting a band is due to one and the same ring of electrons. The number of bands in a group is determined by the number of electron rings. The theory also affords information relative to the distribution of the intensity in the line and band series. From the position of the intensity maximum it is possible to obtain information in regard to the number of electrons in the various rings. H. M. D.

A Simple Sodium Lamp for the Polarimeter. G. FRERICHS (*Chem. Zentr.*, 1916, i, 727; from *Apoth. Zeit.*, 1916, **31**, 94).—Two magnesia troughs as described by Wedekind (A., 1913, ii, 578) are fitted with the concave sides towards one another into the upper edge of a burner chimney so as to lie about 8 mm. apart. One is broken in the middle and sodium chloride fused on to the two halves. The chimney is placed on the star of a bunsen burner, so that the under side of the troughs are about 1—1·5 cm. above the top of the burner tube. A simple tin screen is also described, and the arrangement of the whole is illustrated in the text. G. F. M.

Results of Crystal Analysis. L. VEGARD (*Phil. Mag.*, 1916, [vi], **32**, 65—96).—The crystalline structure of lead and gold and of oxides of the zircon group have been investigated according to Bragg's method by the use of an X-ray spectrometer.

The relative strengths and the positions of the reflection maxima for the face (111) of lead and gold show that the "point-planes" parallel to this face are equal and equidistant, and the observed glancing angles are in almost perfect agreement with the values calculated on the assumption of a face-centred lattice. The lattice of gold and lead is thus found to be identical with that of copper and silver.

The observations made with crystals of zircon (ZrO_2,SiO_2), rutile (TiO_2), and cassiterite (SnO_2) indicate that in the first case the zircon as well as the silicon atoms are arranged in tetragonal lattices of the diamond type. In the case of rutile and cassiterite the metallic atoms are arranged in the form of a simple prism-centred lattice. The tetragonal structure of these minerals is due to the tetragonal arrangement of the oxygen atoms.

The lattice has a sort of molecular structure in which the three atoms of the molecule MO_2 are situated in a straight line (the molecular axis) with M in the central position. The positions of the oxygen atoms are determined when the directions of the molecular axes and the distance between the metallic and the oxygen atoms are known. In all three minerals the molecular axes are similarly arranged, and are always perpendicular to the tetragonal axis. The fact that the molecular distance is different for different central atoms (M) affords support for the view that the atoms in the group MO_2 are chemically bound.

Some experiments with thorite (ThO_2) have shown that this gives no X-ray reflection. This is in agreement with the "metamict" character of the mineral, the substance having become isotropic, although it preserves the external appearance of the crystalline state. H. M. D.

The Properties of Isotopic Elements in the Solid State. K. FAJANS (*Chem. Zentr.*, 1916, i, 649—650; from *Arbieten aus dem Gebiet der Physik, Math. Chemie*, 623—643).—Proceeding from the assumption that the properties of outer electrons of isolated atoms of isotopes are, to a high degree of exactitude, the same, the author shows that, according to Bohr's theory, the required dependence of the oscillation number of the outer electrons on the mass of the core of the atom demands a difference of 16^{-6}% in the case of two lead isotopes of atomic weight 207·1 and 206. Further, the varying structure of the positive core can have only a very small influence on the outer electrons. The atomic volume of isotopic elements must at the absolute zero be the same, the density must therefore be exactly proportional to the atomic weight, and the inter-atomic forces, and therefore also the elastic constants, must be identical. From the equality of the forces and the difference in the masses, it follows that the relation $\nu_1^2 M_1 = \nu_2^2 M_2$ exists between the atomic oscillation number and the atomic weights.

On account of the difference in the oscillation number, the specific heats of the isotopes must be different; in the case of lead the greatest calculated difference amounts to $\frac{3}{4}$%. Above zero, the

atomic volumes should theoretically show an increasing difference; for the two sorts of lead this only amounts at the ordinary temperature to $0{\cdot}7 \times 10^{-3}\%$. At temperatures above absolute zero no difference, likewise, in chemical properties is to be expected. In conclusion, the deductions drawn from the above with reference to the classification of the elements are discussed. G. F. M.

Atomic Weights of the Isotopes Thorium and Ionium. O. HÖNIGSCHMID (*Zeitsch. Elektrochem.*, 1916, **22**, 18—23).—The author has determined the atomic weight of thorium derived from minerals poor in uranium, and of thorium derived from minerals rich in uranium. The latter specimens of thorium contain large percentages of ionium. It has been shown that ionium and thorium are identical in their chemical and physical properties, but that they should have different atomic weights. The present work was undertaken with the object of confirming the theoretical conclusions. The determinations were carried out on the tetrabromide, which was purified in quartz glass apparatus by the method previously used in the determination of the atomic weight of uranium (Hönigschmid, A., 1914, ii, 662; 1915, ii, 635). The ratios $ThBr_4:4Ag$; $ThBr_4:4AgBr$; $(Th{\cdot}Io)Br_4:4Ag$, and

$$(Th{\cdot}Io)Br_4:4AgBr$$

were obtained, twelve experiments being made in the first two cases, and three in each of the last two. The values obtained were: $ThBr_4:4Ag$, 232·152; $ThBr_4:4AgBr$, 232·150, from which $Th = 232{\cdot}151 \pm 0{\cdot}0165$; $(Th{\cdot}Io)Br_4:4Ag$, 231·507; $(Th{\cdot}Io)Br_4:4AgBr$, 231·503, from which $Th{\cdot}Io = 231{\cdot}050 \pm 0{\cdot}0135$. This definitely shows that ionium has an atomic weight which differs considerably from that of thorium. Assuming that ionium has an atomic weight of 230, it would follow that the ionium material analysed contained 30% Io. The atomic weight of thorium, 232·151, differs considerably from the accepted value, 232·4; the author is of the opinion that the lower value is the more correct. J. F. S.

Depolarisation by Electrical Waves. WILDER D. BANCROFT (*J. Physical Chem.*, 1916, **20**, 402—406).—According to Schuster's experiments on disruptive discharge in gases, the electrodes are covered by a film of adsorbed gas which offers an increased resistance to the discharge. The fact that electrical waves diminish the over-voltage is supposed to be connected with the removal of the adsorbed gas layer under the influence of electrical stress. The effect in question may give rise to errors in the measurements of decomposition voltage when these are made by the use of an intermittent direct current, the polarisation being diminished by the induced currents set up at make and break. H. M. D.

Conductivity of Solutions of Certain Iodides in *iso*Amyl and Propyl Alcohols. FREDERICK G. KEYES and W. K. WINNINGHOFF (*J. Amer. Chem. Soc.*, 1916, **38**, 1178—1187).—Dutoit and Duperthuis (A., 1909, ii, 120) have determined the conductivity of sodium iodide in certain alcoholic solvents, and have shown that at low concentrations the law of mass action is obeyed. In view

of Walden's criticism (A., 1912, ii, 23) of these results, a study has been made of the conductivity of sodium iodide in *iso*amyl and propyl alcohols and of ammonium iodide in *iso*amyl alcohol, and the results are in agreement with those of Dutoit and Duperthuis.

In order to keep the solutions free from moisture and other impurities, and to prevent oxidation of the alcohols by the oxygen of the air, the measurements were carried out in a vacuum. The apparatus and method of procedure are described. The equivalent conductivities are given from concentrations ranging from about 0·00005N up to saturation point. It is shown that up to an ion concentration of 0·0004N the electrolytes conform to the law of mass action, and that their conductivity throughout the whole range of concentrations is expressed by Kraus and Bray's equation, $c\gamma^2/1-\gamma=K+D(c\gamma)^m$, where c is the concentration, γ the conductivity ratio Λ/Λ, and K, D, and m are constants (A., 1913, ii, 914). E. G.

The Transference of Electricity by Colloidal Particles. FRANK POWIS (*Trans. Faraday Soc.*, 1916, **11**, 160—163).—It should be possible to calculate the charge on a colloidal particle by determining the conductivity of a colloidal solution of a metal prepared by sparking, as in such a solution the amount of foreign electrolyte is very small, and any conductivity should be due to the transference of electricity by the particles. Taking the values for a silver sol obtained by Burton (A., 1906, ii, 275), the average charge per particle is found to be 2385×10^{-10} electrostatic units, or 795 times that on a univalent ion. As the colloidal solution as a whole is uncharged, if the particles carry a negative charge there must be some positive ions present as well. Calculations are made on this assumption, and give results which are inconsistent with those obtained by the use of Stokes's formula, assuming the mobility of the positive ion to be equal to or less than that of the hydrogen ion. This is the same if the more usual view be adopted, that the ions are adsorbed by the particles. It is now suggested that the particle adsorbs both anions and cations in such a way that the concentration of each decreases gradually with increasing distance from the particle, the anions and cations respectively being in excess at different distances from the particle. The movement of particles under the influence of an electric field is explained on this view. It is, then, not possible to calculate the charge on the particle from the modified Stokes's law, since there is no charge in the usual sense of the term, but the minimum concentration of ions which would be required to give the observed extra conductivity may be calculated (compare Nordenson, A., 1915, ii, 306). C. H. D.

Passivity and Retardation Phenomena during Anodic Discharge of Halogen Ions, and Cathodic Discharge of the Ions of Iron Metals. F. FOERSTER, A. TENNE, F. HERRSCHEL, M. SCHADE, and W. VON ESCHER (*Zeitsch. Elektrochem.*, 1916, **22**, 85—102). —Experiments are described in which the discharge potential of

chlorine ions on platinum anodes from solutions of sodium chloride have been measured. The anodes were both bright and platinised and had been subjected to either anodic or cathodic polarisation before use; the solutions in some experiments were rapidly stirred. It is shown that with moderate current density and a platinised anode, the polarisation slowly increases with the time during which the current is passed. In the case of oxygen-free electrodes, the initial potential is much lower, but rises much more rapidly than is the case with an electrode already charged with oxygen. In the case of an anode cathodically polarised, the potential at first falls, passes through a minimum, and then continuously rises. A similar condition of affairs has previously been observed in the discharge of bromine ions (Foerster and Yamasaki, A., 1910, ii, 576). Similar experiments have been carried out for the discharge of iodine ions from solutions of potassium iodide. A series of experiments on the influence of foreign substances on the cathode potential of the metals iron, cobalt, and nickel has shown that the presence of small concentrations of hydrogen ions ($10^{-5}N$) causes the discharge potential to become much more positive. In the electrolysis of mixed zinc and iron solutions, it is shown that the deposited iron contains small quantities of zinc. The quantity of zinc increases as the current density increases up to a point where the deposition of iron has become so much retarded that the current density cannot be raised sufficiently to effect its deposition at all. In a general theoretical résumé the author characterises two types of passivity: chemical passivity, that is, such passivity as is brought about by catalysts; and mechanical passivity, brought about by protecting layers. J. F. S.

The True Nature of the Supposed Adsorption Potential. R. BEUTNER (*Chem. Zentr.*, 1916, i, 691; from *Elektrochem. Zeitsch.*, 1915, **22**, 177—182).—The electric charge on drops of oil in water is influenced by the addition of salts. This is not caused by the action of surface forces on ions, but depends on the distribution of the salt between oil and water, a certain electrolytic dissociation of the salt in the oil, and the applicability of the osmotic formula for potential differences between oil and water. Independent experimental proof of the intrusion of the salt into the oil was obtained by conductivity determinations, and an estimation of the relative distribution of the salt was likewise possible by this method. G. F. M.

The Differences of Potential at the Contact of Two Electrolytes. G. GOUY (*J. Chim. phys.*, 1916, **14**, 185—194).—A theoretical paper in which formulæ are derived for the potential difference at the surface of contact of solutions of completely ionised electrolytes. H. M. D.

Accuracy of Copper Voltameters. ASWINI KUMAR DATTA and NILRATAN DHAR (*J. Amer. Chem. Soc.*, 1916, **38**, 1156—1160).—Measurements of currents of moderate strength by the copper

voltameter agree with those obtained with the silver voltameter, but in the case of feeble currents lower results are obtained with the copper voltameter than with the silver voltameter (compare Dhar, A., 1913, ii, 917). The present investigation was undertaken with the view of determining the cause of the inaccuracy and the means of obviating it.

It has been found that the experiments may be conducted in an atmosphere of either carbon dioxide or hydrogen, the function being merely to exclude oxygen. The presence of sulphuric acid is necessary to prevent hydrolysis of the copper sulphate, which would lead to deposition of cuprous and cupric oxides on the cathode. It also diminishes the concentration of the copper ions in the solution by increasing the SO_4'' ions and forming complex copper salts, such as $CuH_2(SO_4)_2$. Sucrose or dextrose may be substituted for alcohol in the voltameter, but tartaric acid is better than any of these substances and gives good results even with feeble currents.

Foerster and Seidel (A., 1897, ii, 241) have shown that copper sulphate solutions dissolve copper to an extent depending on the concentration of copper ions in the solution and on the temperature. The good effect of tartaric acid in the voltameter is probably due to the formation of a copper complex and the consequent diminution of the concentration of the copper ions. Reduction of the temperature also diminishes hydrolysis, but in the case of very feeble currents the temperature must not be very low, as the deposition of the copper is thereby rendered so slow that the small concentration of copper ion evolved from the complex is sufficient to vitiate the result slightly by dissolving a little of the freshly deposited copper. E. G.

Application of the Theory of Allotropy to Electromotive Equilibria. IV. A. SMITS and A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1485—1498. Compare this vol., ii, 77).—On the assumption that metal atoms, ions, and electrons are involved in ionisation equilibria represented by $M \rightleftarrows \ddot{M} + 2\odot$ and that such equilibrium conditions obtain in the metal and also in the liquid in contact with the metal, the author arrives at the conclusion that the product of the ion and electron concentrations $[\ddot{M}][\odot]^2$ in the liquid must have a constant value at a definite temperature and pressure. This product is termed the solubility product of the metal.

This conception is made use of in a discussion of the action of water, acids, and halogens on the metals, and an expression is derived for the potential difference at the surface of contact between a metal and solution which is similar to Nernst's equation, but contains a quantity representing the maximum concentration of ions in the metal in place of the electrolytic solution pressure. The electromotive equilibria at the metal-liquid contact surface are examined in terms of this formula, and its applicability to the interpretation of the phenomena of polarisation and passivity is discussed. H. M. D.

Over-voltage and Monatomic Hydrogen. Wilder D. Bancroft (*J. Physical Chem.*, 1916, **20**, 396—401).—In an attempt to explain the phenomena of over-voltage, it is suggested that the electrolytic decomposition of water is essentially an irreversible process, and that intermediate products are formed at the electrodes which are more active chemically than ordinary hydrogen or oxygen. These intermediate products are supposed to be monatomic hydrogen and monatomic oxygen respectively. The over-voltage at the cathode or anode depends on the rate at which the monatomic hydrogen or oxygen is transformed into the ordinary form of the elements. If this rate is small, the over-voltage is high, but if the transformation takes place quickly, the over-voltage is small.

It does not necessarily follow that high over-voltage is accompanied by high reducing or oxidising power, for the normal relations may be disturbed by adsorption phenomena at the electrodes or by specific catalytic effects, by which the rate of the transformation of monatomic hydrogen or oxygen may be greatly increased.

It is shown that the theory affords a plausible explanation of certain peculiarities which have been observed in connexion with the action of sodium amalgam on aqueous solutions, the reducing properties of different samples of zinc dust, and the evolution of hydrogen from a chromous chloride solution. H. M. D.

The Electrolysis of Concentrated Hydrochloric Acid, Using a Copper Anode. F. H. Jeffery (*Trans. Faraday Soc.*, 1916, **11**, 181—182).—The apparatus used is enclosed in a bell jar over water, so that an atmosphere of nitrogen may be kept over the electrodes and solution. The copper dissolves as a complex compound, probably H_2CuCl_3, and cuprous chloride is precipitated. Using potassium chloride in the anode cell and hydrochloric acid in the cathode cell, crystals of the salt K_2CuCl_3 are obtained, showing that the complex anion is $CuCl_3''$. C. H. D.

The Electrolysis of Nitric, Sulphuric, and Orthophosphoric Acids, using a Gold Anode. F. H. Jeffery (*Trans. Faraday Soc.*, 1916, **11**, 172—180. Compare Lenher, A., 1904, ii, 490; Mixter, A., 1911, ii, 613).—When nitric acid (1 : 2) is electrolysed with a gold anode without a porous cell, gold is dissolved to a green solution, and is then reduced by hydrogen, forming a brown precipitate. When a porous cell is used the cathode cell remains clear, but gold is dissolved at the anode to form a solution, which passes from green to deep yellowish-brown. In a vacuum desiccator over sulphuric acid and sodium hydroxide this solution deposits yellow crystals of aurinitric acid,

$$HAu(NO_3)_4,3H_2O.$$

Dilution with water precipitates hydrated auric oxide, the analysis indicating that some aurous oxide is also present. Similar results are obtained with more dilute nitric acid, but the proportion of aurous compound diminishes as the dilution of the acid increases

until with weak acid only auric compounds are formed. This is a good method for the preparation of auric oxide, the only impurity being a little nitric acid. With dilute acid (1:20), if precautions are not taken to prevent the accumulation of ammonium nitrate in the anode cell, a violently explosive compound is formed at the anode.

Gold is also dissolved from the anode in sulphuric acid in the form of complex ions, but by the time the yellowish-brown stage is reached there is an appreciable formation of gold cations. These may possibly arise from the reduction of the anions by hydrogen. The anode solution yields auric hydroxide with a little of the aurous compound on dilution with water.

With a 15% solution of orthophosphoric acid as the electrolyte, a very small quantity of gold goes into solution as complex anions and none as cations. As before, auric and a small quantity of aurous oxides are formed on hydrolysis.

When complex auric compounds diffuse through a porous cell, a part of the gold is precipitated in the form of a purple solid in the porcelain. This is independent of the presence of organic matter. C. H. D.

The Magnetic Susceptibility of Manganese Nitride. TORAJIRÔ ISHIWARA (*Sci. Reports Tôhoku Imp. Univ.*, 1916, **5**, 53—61).—The nitride is prepared by heating aluminothermic manganese, having the magnetic susceptibility $9{\cdot}66 \times 10^{-6}$, in dry nitrogen or ammonia at various temperatures. When nitrogen is used, three ferromagnetic substances are obtained within the range 600—1000°, namely, a nitride, Mn_5N_2, a second nitride of undetermined composition, and a solid solution. The existence of a ferromagnetic compound, Mn_7N_2 (Wedekind, Veit, and Fetzer, A., 1911, ii, 985), has not been confirmed. All these substances give characteristic thermomagnetic curves. Ammonia gives similar products, but also forms a paramagnetic nitride, Mn_3N_2. The varying values for the magnetic susceptibility of manganese given by different investigators are to be attributed to the presence of varying quantities of nitride in the metal. C. H. D.

The Decrease in the Paramagnetism of Palladium caused by Absorbed Hydrogen. H. F. BIGGS (*Phil. Mag.*, 1916, [vi], **32**, 131—140).—The experiments described were designed to throw light on the magnetic properties of hydrogen. Previous observations on the influence of absorbed hydrogen on the magnetic susceptibility of palladium by Graham (*Proc. Roy. Soc.*, 1869, **17**, 212, 500) appeared to indicate a considerable increase in the paramagnetism. This is contrary to the results of the author's measurements, which show that palladium tends to become diamagnetic as the amount of absorbed hydrogen increases.

The data obtained cannot be satisfactorily accounted for on the assumption that the observed effect is the algebraic sum of the diamagnetism of hydrogen and the paramagnetism of palladium. It is probable, on the other hand, that the effect

is due to some interaction between the hydrogen and the metal whereby the paramagnetism of the palladium is reduced.

H. M. D.

Magnetic Susceptibility of Salts in Organic Solvents. Factors which Determine the Susceptibility of Solutions. A. QUARTAROLI (*Gazzetta*, 1916, **46**, i, 371—403. Compare A., 1915, ii, 141; this vol., ii, 123).—Various facts indicate that the magnetic susceptibility of paramagnetic salts is influenced by their state of dissociation, although the character of such influence is not completely explained. The author has made measurements of the susceptibility of various paramagnetic salts in organic solvents, the results leading to the following conclusions.

Using fields varying from 6000 to 32,000 gauss, appreciable diminutions of the susceptibility occur in all cases as the intensity of field increases. With increasing dilution of the solution, in most cases the susceptibility first increases appreciably, then remains constant over a short region, and finally decreases, without, however, tending towards a fixed limit; in general, the maximum value with an organic solvent occurs at a lower concentration than is the case with an aqueous solution. The values of the susceptibility are in every instance higher than in water under similar conditions of concentration. The numbers of magnetons are, on the whole, markedly superior to those obtained in water, and eleven out of a total of twenty-one answer theoretical requirements if the limit of error assumed by Weiss is adopted. The value of the magneton theory in its application to solutions is regarded as doubtful. The value of the susceptibility of a solution appears to depend, not merely on the actual susceptibilities of the magnetic ions and of the undissociated molecules, but also on the movement of the solute in the solvent under the action of the magnetic field, even though this may escape direct observation.

T. H. P.

Crystallisation in a Magnetic Field. ARNE TVETEN (*Physikal. Zeitsch.*, 1916, **17**, 235—237).—Solutions were allowed to crystallise on watch- or cover-glasses between the poles of an electromagnet, the strength of the field varying between 500 and 4500 gauss. The growth of the crystals was watched through a microscope. Most of the observations were made with a solution prepared by mixing equal volumes of a 30% solution of ferrous ammonium citrate and of a 10% solution of potassium ferricyanide. After filtration, sodium hydroxide was added, and the precipitate formed was redissolved by addition of a little tannin. Ammonia was then added until the solution turned red. When this solution crystallises in the magnetic field, tables or leaf-like forms appear on the outskirts of the field, but in the middle, needles, with their length perpendicular to the lines of force. Soon after the magnetic field has been destroyed the needles break up. They oxidise in air, becoming blue, and the magnetic field appears to accelerate this change.

Potassium ferricyanide crystallised in a magnetic field from a supersaturated solution forms prisms, their length perpendicular to the lines of force, but from an ordinary saturated solution it forms rhombs having one diagonal parallel to the lines of force.

E. H. R.

Law of Thermal Expansion of Liquids. ALFRED ALBERTOSI (*J. Chim. phys.*, 1916, **14**, 176—177).—In a previous paper (compare this vol., ii, 214) the relation $d^{5/3}=A-Bt$ connecting the density d with the temperature t was derived, and it was erroneously stated that the constant A represents the density of the liquid at the absolute zero. It is now pointed out that this density is given by $A^{3/5}$.

The formula has been further tested, with satisfactory results, by application to the data for mercury between $-20°$ and $300°$, and for hexahydronaphthalene between $13°$ and $173°$. H. M. D.

[**Law of Thermal Expansion of Liquids**]. MAURICE PRUD'HOMME (*J. Chim. phys.*, 1916, **14**, 180—184).—The relation $d^{5/3}=A-Bt$, connecting the density with the temperature (compare Albertosi, preceding abstract), is found to be in satisfactory agreement with the data for amyl acetate, aniline, and *m*-xylene.

For amyl acetate, the variation of the surface tension γ with the temperature t is found to accord with the formula $\gamma^{2/3}=A-Bt$, in which A and B are constants. H. M. D.

The Latent Heat of Fusion of a Metal and the Quantum Theory. H. STANLEY ALLEN (*Proc. Physical Soc. London*, 1916, **28**, 204—209).—According to the quantum theory, the latent heat of fusion of a crystalline solid may be identified with the energy which is necessary to counterbalance that of a certain number of oscillators which are involved in the maintenance of the crystalline structure. It is shown that the latent heat of fusion of a gram atom of a metal can be approximately calculated on the basis of the quantum theory if it is assumed that the latent heat corresponds with the energy of oscillators the frequency of which at the melting point is given by Lindemann's formula. The calculations for a number of metals indicate that the number of oscillators in each atom is in many cases equal to one, and in all cases less than two. H. M .D.

Physical Properties of Gases in Relationship to their Boiling Points. A. IMHOF (*Zeitsch. physikal. Chem.*, 1916, **91**, 431—440).—The author has previously published (A., 1916, ii, 218) an account of the relationship between the solubility of gases in water and their boiling points. This connexion is now found to hold for the solubility in liquids other than water. The relationship $a=e^{(T-\tau)/\lambda}$ represents the connexion between the two quantities, where a is the absorption coefficient, T the absolute temperature of the boiling point, τ and λ specific constants for the solvent in question. The above expression is for the normal pressure,

760 mm.; if the pressure p is considered, then $a_p = e^{(T-\tau)/\lambda + \log p}$. A number of other properties of gases have been considered in the above-mentioned connexion. The relationship between the boiling point (T) and the mean free path (L) is given by

$$L(\text{cm.}) = 2{\cdot}5 \times 10^{-5}/(1 + 0{\cdot}016T),$$

that between the molecular surface per c.c. (Q) and the boiling point is given by $Q = (1 + 0{\cdot}016T)10^4/\sqrt{2}$, and that between the coefficient of refraction and the boiling point by

$$n - 1 = x(1 + 0{\cdot}016T),$$

where n is the index of refraction and $x = 1/8000$ for white light. Further relationships are indicated by curves between the boiling point on the one hand and the discharge potential and the coefficients of expansion of gases by heat and by reduction of pressure on the other. J. F. S.

Receiver for Vacuum Distillations. J. J. PLONSKIER (*Zeitsch. angew. Chem.*, 1916, **29**, i, 212).—The stem of a **Y**-shaped tube is attached to the lower end of the condenser; a short side-tube on the stem is connected with a pump, and the arms of the **Y**-tube are each provided with a three-way tap. Small collecting vessels are attached to the ends of these arms by means of rubber stoppers. When the desired quantity of distillate has collected in one of these vessels, the **Y**-tube is rotated, the tap on the arm leading to the vessel containing the distillate is turned so as to admit air and cut off connexion with the condenser, the tap on the other arm being meanwhile turned so that the distillate can collect in the second vessel. W. P. S.

The Condition of Substances in the Interior of the Sun. E. BRINER (*J. Chim. phys.*, 1916, **14**, 178—179).—Although the temperature of the sun is in all probability very much higher than the critical temperatures of the least volatile liquids, from which it follows that liquid substances cannot exist in the sun, the author suggests that this temperature may not be incompatible with the existence of solid substances under high pressures.

Reference is made to the observation that phosphonium chloride exists as a solid at temperatures above 100°, although the critical temperature of the liquid is 49·1°. It is also noteworthy that Bridgman has found that carbonic acid exists in solid form at temperatures above the critical temperature (31°) when the pressure is of the order of 6000 atmospheres. H. M. D.

Modified Victor Meyer Apparatus. HARRY B. WEISER (*J. Physical Chem.*, 1916, **20**, 532—538).—A modified form of the Victor Meyer vapour density apparatus is described in the paper. The chief advantage of the modification lies in the fact that the apparatus is more compact. This is achieved by causing the ordinary connecting neck of the old apparatus to project through the bottom of the bulb to about three-quarters of the length of the bulb. The connecting tube is bent parallel with the bulb, and higher up is connected with a capillary tube. Both the

bulb and neck are placed inside the heating jacket. The material is introduced by a short tube at the end of the bulb. This short length of tube is fitted with a rubber stopper, which carries a capillary stopcock. The results of experiments effected by means of this apparatus compare favourably with those determined by means of the original apparatus. J. F. S.

The Law of Distribution of Molecular Velocities and the Theory of Viscosity and Thermal Conduction, in a Non-uniform Simple Monatomic Gas. S. CHAPMAN (*Phil. Trans.*, 1916, [*A*], **216**, 279—348).—A theoretical paper, in which the mode of distribution of velocity amongst the molecules is considered and equations obtained for the viscosity and thermal conductivity on the assumption that the molecules consist of (*a*) rigid elastic spheres, (*b*) attracting spheres, (*c*) centres of force. The formulæ are compared with those obtained on the basis of other assumptions and with the results of experimental observations. H. M. D.

Surface Tension of Fresh Surfaces of Pure Water and Salt Solutions. G. MEYER and H. STOCKER (*Zeitsch. Elektrochem.*, 1916, **22**, 5—11).—The surface tension of pure water and a number of salt solutions has been calculated by the Rayleigh and Bohr formulæ from measurements of the wave-length of a stream of the liquid flowing from an elliptical capillary tube. The other data required were the velocity of efflux of the solution and the radius of the stream at the crests and nodes. An optical method is described for determination of the wave-length, and the radii were measured directly by means of a microscope and micrometer. The results show that with fresh surfaces the surface tension of water and salt solutions is approximately 0·5 dyne/cm. smaller than for old surfaces. The surface tension is increased by the addition of salts to water when the measured surface is continually renewed. J. F. S.

Adsorption by Charcoal in Alcoholic Solutions. BROR GUSTAFSON (*Zeitsch. physikal. Chem.*, 1916, **91**, 385—409).—With the object of ascertaining whether or no an adsorption maximum was obtainable from alcoholic solutions, the author has investigated the adsorption of benzoic acid, picric acid, and phenol from alcoholic solution by animal charcoal at 25°. A further series of experiments on the adsorption of the vapours of phenol, water, and alcohol by charcoal has also been carried out. In the case of benzoic acid it is shown that the value of $u_0(1-c)$ reaches a maximum with a 1·3*N*-solution, whilst u_0 increases with the concentration when calculated by the Schmidt formula. The Freundlich formula is also non-applicable to benzoic acid, for at small concentrations the logarithmic curve is strongly convex to the $\log c$ axis for small concentrations. Freundlich's formula expresses the experimental results for small concentrations of picric acid, but at higher concentrations the λ value in the formula $\lambda = v/m \log_e a/(a-x)$ shows a decided increase with the quantity of charcoal. The diver-

gence at high concentrations is in accordance with the theory of adsorption-reversal. No tendency to the formation of solid solutions is observed, as was the case in Georgievic's experiments on the adsorption of picric acid by silk (A., 1911, i, 537; 1912, ii, 140). In the case of phenol it is shown that the u_0 value reaches a maximum value and then falls. The experiments with vapours did not furnish the true adsorption as was hoped; in the case of alcohol vapour no definite result was obtained, whilst in a case of phenol a saturation was reached, but only after a year. From the experimental results of Williams (A., 1914, ii, 111) it is shown that the adsorption of the dissolved substance is in keeping with a driving back of the adsorption, and this follows the Freundlich formula. This formula expresses the adsorption of acetic acid by charcoal when the concentration is changed from 0·00003 to 0·7, that is 23,000 times, and also when the adsorption varies from 0·007 to 0·412, that is 60 times. J. F. S.

Simultaneous Adsorption by Two Adsorbing Media. G. VON GEORGIEVICS (*Zeitsch. physikal. Chem.*, 1916, **91**, 441—442).—Polemical. It is pointed out that the experiments of Lachs (this vol., ii, 226) are not, as claimed by the author, the first of the type in question, but that many such have been studied in connexion with the dyeing of silk-wool, silk-cotton, and wool-cotton mixtures.

J. F. S.

Dissociation of Hydrogen into Atoms. III. The Mechanism of the Reaction. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1916, **38**, 1145—1156).—In an earlier paper (A., 1915, ii, 249) the dissociation of hydrogen into atoms was calculated from the results of experiments on the losses of heat from tungsten wires in hydrogen at various pressures (Langmuir and Mackay, A., 1914, ii, 717). For the purpose of this calculation, it was assumed that the surface of the wire contained atoms and molecules of hydrogen in chemical equilibrium with each other, and that the atoms and molecules escaped from the wire at rates respectively proportional to their concentration in the wire, whilst the absorption of the atoms or molecules by the wire was regarded as proportional to the corresponding pressures in the gaseous phase. It is now shown that there are certain objections to these assumptions, and a new theory has therefore been developed, in which these objections do not arise. The new theory leads, however, to the same equation which was derived in the previous paper (A., 1915, ii, 249).

The velocity of the reaction by which hydrogen is dissociated in contact with a heated tungsten wire is so enormous that it is impossible that it can depend on a diffusion of the hydrogen into the metal even if the depth of penetration were only that of a single atom. In the new theory it is assumed that the reaction takes place in the actual surface layer of atoms, and that the hydrogen evaporates so rapidly from the surface that only a negligible fraction of the surface is covered at any time. The latter assumption accords with the fact that the accommodation coefficient

of hydrogen is 0·19 at temperatures below 1500° (abs. temp.), whilst the chemical coefficient, α_2, for the dissociation is 0·68 at high temperatures (*loc. cit.*), and it is supported by the fact that the electron emission from tungsten is not perceptibly influenced by the presence of pure hydrogen (A., 1914, ii, 412). E. G.

Dissociation of Gaseous Acetic Acid and Phosphorus Pentachloride. Correction. W. NERNST (*Zeitsch. Elektrochem.*, 1916, **22**, 37—38).—The author gives corrected calculations of the work of C. Holland (*ibid.*, 1913, **18**, 234). It is shown that the heat of dissociation is expressed by the equations: $K_p = 15000/4{\cdot}57T - 1{\cdot}75 \log T - 3{\cdot}88$ for acetic acid and $K_p = 20000/4{\cdot}57T - 1{\cdot}75 \log T - 3{\cdot}78$ for phosphorus pentachloride. The degree of dissociation of both substances is calculated for temperatures between 413° and 623°. J. F. S.

An Inexpensive Dialyser for Class Use. HARRY N. HOLMES (*J. Amer. Chem. Soc.*, 1916, **38**, 1204—1205).—An inexpensive dialyser of the shape of a beaker can be made by folding a piece of parchment paper, previously softened by soaking it in water, over a bottle of the desired size and shape. The folds should be triangular and creased with firm pressure. A piece of twine is tied round the parchment and bottle, about 1 cm. from the upper edge, and when the parchment is dry it is removed. The twine is left on the cup to support the sides. Such a parchment cup retains its shape well, and may be provided with a handle by punching a hole in each side near the top and attaching a piece of string. Since the whole of the cup forms an effective dialysing surface, dialysis proceeds rapidly when the cup is filled with a colloidal solution and placed in a large vessel of water. To increase the rate of dialysis still further, a smaller parchment cup containing water may be placed inside the larger one. E. G.

A Recalculation of some Work on Diffusion. A. GRIFFITHS (*Proc. Physical Soc.*, 1916, **28**, 255—257. Compare this vol., ii, 88).—The data obtained in experiments on the diffusion of potassium chloride in aqueous solution have been subjected to a re-calculation. The results obtained for the coefficient of diffusion by three different methods of experiment are now found to agree within the limits of experimental error. H. M. D.

Solubilities of Several Substances in Mixed Non-aqueous Solutions. J. W. MARDEN and MARY V. DOVER (*J. Amer. Chem. Soc.*, 1916, **38**, 1235—1245).—The solubilities have been determined at 25° of acetanilide, strychnine, benzoic acid, and iodine in mixtures of ether and chloroform in varying proportions, of acetanilide and benzoic acid in mixtures of acetone and benzene, and of benzoic acid in mixtures of ethyl acetate and benzene.

It has been found that the solubilities in mixtures of ether and chloroform are exponential functions of the percentage composition of the solvent, and that the law governing the fractional precipita-

tion may be stated in the same way as the law of distribution. In only one case, that of acetanilide in a mixture of benzene (10%) and acetone (90%), was the solubility greater than in either of the pure liquids. When the solubilities are plotted against the percentage concentration of one of the components of the mixed solvent, smooth curves are usually obtained, but broken curves are obtained with acetanilide in acetone-benzene solutions, with benzoic acid in acetone–benzene solutions, and with benzoic acid in ethyl acetate–benzene solutions. It is suggested that such irregularities may be due to the formation of compounds with the solvent similar to the hydrates formed in aqueous solutions, such compounds being decomposed when the solid material is precipitated by addition of the poorer solvent. E. G.

Supersaturated Solutions of Liquids in Liquids. HAROLD S. DAVIS (*J. Amer. Chem. Soc.*, 1916, **38**, 1166—1178).—Attempts to obtain supersaturated solutions of liquids in liquids have hitherto met with but little success. Experiments have now been made to determine the degrees of supersaturation in water of phenol, aniline, nitrobenzene, and carbon disulphide, and definite evidence of supersaturation has been obtained with the last two substances. The method employed was similar to that used by Rothmund (A., 1898, ii, 503), consisting in the determination of the difference between the temperatures at which mixtures of known composition become turbid on cooling and clear on heating. An attempt is made to explain the phenomena observed on the basis of existing theories.

The solubility of nitrobenzene in water (grams per 100 grams of solution) is 0·19 at 20°, 0·22 at 30°, and 0·27 at 55°, and that of water in nitrobenzene is 0·174 at 8·8°, 0·194 at 14·7°, 0·299 at 30·8°, 0·401 at 44·2°, 0·713 at 63·3°, and 1·53 at 106·6°. The solubility of carbon disulphide in water decreases as the temperature rises from 0° to 50°, and subsequently increases. E. G.

Assumption of Micellæ is Superfluous for the Explanation of Uncomplicated Swelling by Imbibition. J. R. KATZ (*Zeitsch. physiol. Chem.*, 1915, **96**, 255—287).—The changes in the aqueous vapour pressure of caseinogen, cellulose, tricalcium phosphate, gum arabic, peptone, serum-albumin, and cerebrin occurring during the imbibition of water have been compared with similar changes occurring on mixing sulphuric acid, phosphoric acid, and glycerol with water. On expressing the results graphically, the same type of curve is obtained from the imbibition as from the mixing experiments. The estimation of the heat developed during imbibition is also of the same order as that developed during mixing, and again the same type of curve is obtained from the two sets of experiments. Analogous results are also afforded by the measurement of the contraction in volume of the substances concerned in each case; hence the conclusion that imbibition is merely the process of solution of water in the swelling substance. In other words, during imbibition water passes, not between

micellæ, but between molecules of the substance absorbing the water. H. W. B.

The Growth of Crystals under External Pressure. STEPHEN TABER (*Amer. J. Sci.*, 1916, [iv], **41**, 532—556).—It was shown by Becker and Day (A., 1905, ii, 807) that crystals of alum and other substances could be caused during growth to raise a weight of a kilogram several tenths of a millimetre. Bruhns and Mecklenburg (6th Jahresb. Niedersächsischen geol. Vereins, 1913, 92—115) repeated these experiments with negative results, and the author now shows that their failure is to be attributed to the fact that they attempted to grow weighted and unweighted crystals together in the same vessel. The fact that a crystal will grow downwards from its under surface, thereby exerting a force by which it can raise itself and even a considerable additional load, is intimately connected with the formation of a stepped hollow on its under surface. Experiments are described which demonstrate conclusively that downward growth takes place by addition to the outer rim of the under surface only, the centre of the face being gradually raised, but no material being deposited on it. The outer rim, bearing the whole of the weight, is under considerable pressure, by which its solubility is increased. It follows that the thin layer of solution between the rim and the bottom of the vessel must become considerably supersaturated with regard to faces not under pressure before it can deposit material on the under face. The presence of unweighted crystals in the same solution as weighted ones, as in Bruhns and Mecklenburg's experiments, would prevent the bottom layer of solution from ever becoming supersaturated with regard to the under faces of the latter.

Experiments are described by means of which the growing force of crystals is made to shatter a glass bulb and a porous pot. The influence of external conditions on the manner of growth of crystals is discussed, together with the geological significance of observations made in the laboratory. E. H. R.

Theory of Allotropy. J. W. TERWEN (*Zeitsch. physikal. Chem.*, 1916, **91**, 443—468).—A theoretical paper in which the present and past theories of allotropy are considered critically.

J. F. S.

The Viscosity of Colloidal Solutions. EMIL HATSCHEK (*Proc. Physical Soc. London*, 1916, **28**, 250—254).—In discussing the viscosity of colloidal solutions, Hardy (*ibid.*, 99) has criticised the view put forward by Einstein and by Hatschek maintaining that the relations required by this theory are only satisfied in the case of the simplest hydrosols and suspensions.

The author, in reply, points out that no viscosity formula is applicable to systems which have many of the properties of an elastic solid, and that the formula deduced by Einstein and himself for the viscosity of a suspension of rigid spherical particles

does not apply to systems which belong to the emulsoid group. For emulsoid systems a totally different formula has been derived, and this has received a considerable amount of experimental support. The fact that the degree of solvation and the swelling of indiarubber in different solvents are proportional is also in favour of the theory underlying the second formula. H. M. D.

Colloidal Solutions and Organic Syntheses. M. Bakunin (*Ann. Chim. Applicata*, 1916, **5**, 243—251).—Small proportions of the three nitrobenzylidene diacetates are obtained as secondary products in the synthesis of the phenylnitrocinnamic acids by Perkin's method from sodium phenylacetate, acetic anhydride, and the three nitrobenzaldehydes (see Bakunin and Parlati, A., 1906, i, 664). It is now found that this secondary reaction is determined, and in some cases rendered almost quantitative, by the presence of colloidal solutions of various compounds in acetic anhydride. Among such compounds are phosphoric oxide, ferric oxide, sulphur trioxide, zinc chloride, and phosphorus pentachloride, the action of the first being almost instantaneous. It appears possible that other catalytic organic reactions may represent the results of the formation of colloidal solutions.

T. H. P.

Reactions of Colloidal Gold. Richard Zsigmondy (*Zeitsch. Elektrochem.*, 1916, **22**, 102—104).—It has previously been shown that colloidal gold, like many other colloidal substances, is coagulated when shaken with organic solvents such as choloroform, benzene, and other liquids, which are non-miscible with water. The present paper deals with this phenomenon and furnishes an explanation. The above-mentioned results are directly opposed to the results of the author's experiments. If a bright red colloidal solution of gold is shaken with pure benzene, toluene, or ether in glass-stoppered bottles there is no coagulation, even if the shaking is carried on for eighty hours, but if the shaking takes place in a test-tube closed by the finger there is instantaneous coagulation. Similarly, impure ether effects the precipitation instantaneously in glass bottles. If the ether has been shaken with alkali hydroxide, then no coagulation occurs with the gold sol prepared with formalin, but when the sol is prepared by the Donau method coagulation still occurs in glass bottles. The addition of a trace of acid to the formalin sol causes it to coagulate on the addition of an organic solvent. The reason for the coagulation when the mixture of sol and organic solvent is shaken in a test-tube closed by the finger is shown to be that an albuminous substance is dissolved from the skin, and this effects the coagulation. Experiment confirms this, for gelatin, casein, peptone, and albumin effect the same coagulation even when present in traces, whereas dextrin, rubber, and similar protective colloids have no such action. The explanation of the action of these substances is that gold is a positive sol, whilst these substances are negative sols; the isoelectric point lies in the region of $10^{-5}N$ H ions, so

that the coagulation of the two substances is a mutual one. The influence of the size of the colloidal particles is discussed.

J. F. S.

Washing Precipitates for Peptisation. HARRY N. HOLMES and R. E. RINDFUSZ (*J. Physical Chem.*, 1916, **20**, 522—527).—Great difficulty is often experienced in the preparation of precipitates for peptisation, owing to the difficulty of removing adsorbed electrolytes. The authors have compared four methods of removing electrolytes from precipitated ferric arsenate. The methods are: (i) simple washing on the filter; (ii) repeated shaking of the precipitate with water and decanting; (iii) washing by decantation without shaking; and (iv) repeated shaking with water and sand and then decanting. In each case the filtrate was analysed to ascertain the quantity of excess potassium arsenate which had been removed. The efficacy of the four methods is shown by the following figures. The total quantity of excess potassium arsenate is represented by 1·4371 grams of arsenic, after twenty washings, each time using the same volume of water: 1·3983 grams of arsenic were removed by (i), 1·4118 by (ii), 1·2943 by (iii), and 1·4324 by (iv). It therefore follows that for approximate freedom from electrolytes simple washing of the precipitate is sufficient, whilst for absolute freedom from electrolytes shaking with sand is to be recommended. J. F. S.

Non-, Uni- and Bi-variant Equilibria. VIII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1539—1552. Compare this vol., ii, 231, 381).—A further consideration of certain properties of the equilibrium diagrams which have been discussed in previous papers of this series. H. M. D.

Reaction Kinetics and Additive Nature of the Internal Heat of Ideal Gases. MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1916, **22**, 104—107).—Commencing with the general thermodynamic equation for the velocity of chemical reactions of the $\Sigma\nu$ order, $k = xe^{-q_0/RT - \Sigma\nu/WdT/RT^2 - 1}$, which has previously been considered (*Sitzungsber. Heid. Akad.*, 1915, 2), the author deduces the special equations for reactions of the first, second, and third order. A general statement, characterised as the substance stability rule, is established which has the form "that reactions are only of the first and second order." In the case of the formation of NOCl (see Trautz, A., 1915, ii, 338), it is shown that in order that this reaction may be demonstrated as of the third order $NOCl_2$ must be formed as a primary product; this formation is found to be represented by $\log K_{NOCl_2} = 390{\cdot}5/T + 1{\cdot}5 \log T - 6{\cdot}7$. A general discussion of the conditions demanded, particularly in the case of NOCl, for the acceptance of the additive character of the internal heat concludes the paper. J. F. S.

Combination of Chlorine and Hydrogen. M. BODENSTEIN (*Zeitsch. Elektrochem.*, 1916, **22**, 53—63).—A number of experi-

ments have been carried out with the object of comparing the influence of α-rays and of heat on the combination of hydrogen and chlorine with that of light on the same reaction. In the case of α-rays, a small bulb of radium emanation was placed in the centre of a larger bulb containing a mixture of chlorine and hydrogen, and of such dimensions that the whole of the α-rays were absorbed. Small quantities of the gaseous mixture were removed from time to time and analysed. The results of the experiments show that the velocity of combination can be represented by the equation $dx/dt = kJ_{abs}[Cl]/[O_2]$, in which J_{abs} represents the quantity of α-rays absorbed. In the case of thin layers of the gas, $dx/dt = kJ_0[Cl_2]^2/[O_2]$ gives the velocity of the reaction. Further, $dx/dt = k . Em . G . [Cl_2]/P$. In all respects the results agree with those obtained for the action of light on a mixture of chlorine and hydrogen, and are completely in accord with the theory of the mechanism of the action put forward in connexion with this work (A., 1913, ii, 1039). As the result of recent work by Lenard, Ramsauer and Ludlam (A., 1912, ii, 511), and J. J. Thomson (*Proc. Camb. Phil. Soc.*, 1901, **11**, 901), the author has been compelled to abandon his theory of the action as untenable. A further theory is put forward, which, like the former one, assumes both a secondary and a primary reaction, but, instead of assuming a splitting of the molecules before reaction into a residue and an electron, assumes that the molecule is activated by the absorption of light energy. This activation is assumed to consist in a loosening of the valency electrons in the same manner as is predicated in Stark's hypothesis. These activated molecules (Cl_2 in the present case) react readily with hydrogen, and produce hydrogen chloride with loosened electrons. When these molecules collide with chlorine molecules they activate these by imparting their high vibration period.

The velocity of reaction by warming is given by the equation $d[2HCl]/dt = k . [Cl_2][H_2]/[O_2]$. J. F. S.

Gaseous Combustion. W. A. BONE (*Rep. Brit. Assoc.*, 1915, 368—385).—Presidential address to Section B (Chemistry). The subject is dealt with under the following heads: Ignition phenomena; the influence of electrons on combustion; the initial period and limits of inflammability; the combustion of hydrocarbons; fuel economy and the proper utilisation of coal. C. H. D.

The Reaction of both the Ions and Molecules of Acids, Bases, and Salts. W. A. TAYLOR and S. F. ACREE (*J. Physical Chem.*, 1916, **20**, 353—395. Compare A., 1915, ii, 681).—Further measurements have been made of the velocity of the reaction between sodium ethoxide and methyl iodide in ethyl-alcoholic solution at 0°. The calculated molecular and ionic activity coefficients are in good agreement with those obtained previously.

The data obtained by Hecht, Conrad, and Brückner (*Zeitsch. physikal. Chem.*, 1890, **5**, 289) in their work on the velocity of reaction between sodium ethoxide and alkyl haloids at different

temperatures have been recalculated in terms of the theory of dual catalysis with satisfactory results. In terms of the dual catalytic hypothesis, the constant a in the empirical equation used by the above investigators, namely, $K' = K + a \log V'/V$, assumes the form $a = (K_i - K_m)(\alpha' - \alpha)/\log V'/V$, in which K_i and K_m are the velocity coefficients for the ionic and molecular reaction, α' and α the degrees of ionisation of sodium ethoxide at volumes V' and V respectively. H. M. D.

Alcoholysis of Salts. H. GOLDSCHMIDT (*Zeitsch. Elektrochem.*, 1916, **22**, 11—15. Compare A., 1915, ii, 214).—The author has developed theoretically the conditions of alcoholysis of salts in absolute alcohol solution. It is shown that the addition of water to the alcohol has the effect of driving back the alcoholysis. To test these deductions, the degree of alcoholysis of aniline salicylate, aniline trichlorobutyrate, *p*-toluidine salicylate, *o*-toluidine salicylate, and *o*-toluidine dichloroacetate has been determined in absolute alcohol solution and in alcohol-water mixtures of varying composition. The experimental method adopted is indirect, and consists in measuring the electrical conductivity of the sodium salt of the acid in question and plotting the change of conductivity with dilution on a curve. The mixture of organic base and acid is then similarly measured, and the dilution at which the sodium salt has this conductivity is obtained from the curve. In this way the amount of salt of the base present at this dilution is obtained. This method is justified by the author on the ground that the aniline ion and the sodium ion have almost the same ionic conductivity (47 and 48 respectively), and that although the degree of dissociation is not the same in the two cases, when weak acids are used, as in the present case, the difference in the degree of dissociation is of little importance. J. F. S.

Effect of Dissolved Substances on the Velocity of Crystallisation of Water. II. Existence of Hydrates in Solution as an Explanation of the Retarding Effect of the Solute on the Velocity of Crystallisation of Water. JAMES H. WALTON and ALBERT BRANN (*J. Amer. Chem Soc.*, 1916, **38**, 1161—1166).—In an earlier paper (this vol., ii, 233) a relation was pointed out between the retardation of the velocity of crystallisation of supercooled water by a dissolved substance and the number of atoms in the molecule of that substance. An extension of the work has shown that this relation does not always hold, and that in the cases previously studied it was probably largely accidental.

The experiments now described show that substances which undergo the greatest hydration in solution show the greatest retarding effect on the velocity of crystallisation of water in supercooled solutions, and this affords an explanation of the earlier results. If the formation of ice crystals is due to some such change as $3(H_2O)_2 \rightleftharpoons 2(H_2O)_3$, it is evident that any part of the solvent in combination with the solute would have to be decomposed before crystals could be produced, and consequently crystal-

lisation in a solution containing a hydrated solute would be much slower than in the pure solvent. In dilute solutions the retardation is almost entirely due to the existence of hydrates, but in concentrated solutions other factors play an important part. In solutions as dilute as $0{\cdot}1M$ there is a marked difference between the effect of substances which are hydrated and of those which undergo hydration to only a very slight extent. E. G.

Sabatier's Catalytic Actions. UGO GRASSI (*Nuovo Cim.*, 1916, [vi], **11**, i, 147—163).—The author has investigated the hydrogenation of ethylene in presence of recently reduced copper at various temperatures between 150° and 300°. The catalyst at first exhibits variable activity, but gives constant and reproducible results after it has been subjected for several hours to the action of a circulating mixture of ethylene and hydrogen at 250°. The thermostat and thermoregulator were charged with dense automobile oil, which exhibits sufficient mobility at temperatures above 50° to admit of uniform distribution of the temperature.

The mean values of the initial velocities of the hydrogenation at different temperatures are as follows: 150°, 0·25; 200°, 1·10; 250°, 1·19; and 275°, 1·21. The velocities of the reaction are found to be rigorously proportional to the concentrations of the hydrogen and ethylene, and the conclusion is drawn that the reaction is of the type of absorption reactions. The anomalous values of the temperature coefficient of the reaction, which should be about 2, but is low at 150—200°, and lower still at higher temperatures, are explainable according to Trautz's theory of the influence of temperature on the velocity of reaction (A., 1910, ii, 24; 1912, ii, 746). This theory leads to the result that the temperature at which the maximal velocity of a reaction is reached becomes lower as the heat of formation from the elements of the system diminishes; in the present case the heats of formation of ethane and ethylene are +23,300 and −14,600 cals. respectively, and the maximal velocity is attained or approached at 275°. The hydrogenation of propylene should exhibit the same phenomenon, but to a less marked degree. T. H. P.

A New Arrangement of the Periodic System of the Elements. HUGO STINTZING (*Zeitsch. physikal. Chem.*, 1916, **91**, 500—507). —The system is a modification of the Werner system, with the difference that similar sub-groups are brought together. Eight periods are represented and provided for in the arrangement, namely, an unknown period, a preperiod containing 3 members, two short periods of 17 elements, two medium periods of 45 elements, and two long periods of 87 elements. This system of representation arranges the elements in positive and negative subgroups; certain unsymmetrical characters allow of the complete inclusion of the radio-elements, the rare earths, and the eighth group of the ordinary method of representation. A complete separation of the metals from the non-metals is possible in the present arrangement. J. F. S.

The Position of the Abundant Elements in the Periodic System. JOHN WADDELL (*Chem. News*, 1916, **113**, 289—290).—Attention is drawn to the existence of a relation between the atomic weights of the elements and the relative quantities in which they occur in nature. For the most part, the elements in the typical series are found in greater abundance than other elements which belong to the same group. Oxygen is quite exceptional in this respect, but argon is only anomalous if regarded as the first member of the third series. It may, however, equally well be regarded as the last member of the typical series.

In a discussion of the relationships which are exhibited, the author lays stress on the necessity for explaining the comparatively small quantity of elements of high atomic weight and the small quantity of elements of lowest atomic weight. If the elements are products of disintegration, it would seem that the gaseous stars and nebulæ represent later stages than the sun in the evolutionary process, which is contrary to the view usually held. To account for the abundance of oxygen, it is suggested that it represents the end product of the disintegration of a large number of elements.

H. M. D.

A Crucible "Fork." H. G. PARKER (*J. Amer. Chem. Soc.*, 1916, **38**, 1203—1204).—A "fork" is described which is made of stout aluminium wire, the two prongs enclosing slightly more than a semi-circle and being bent to fit the crucible. The distance between the ends of the prongs should be so adjusted as to allow the prongs to pass round the crucible when supported on a triangle and to prevent the crucible from slipping through when lifted.

E. G.

Two New Lecture Experiments. A. KÜNG (*Chem. Zeit.*, 1916, **40**, 511—512).—To demonstrate the volume relationships between nitric oxide and dissociated and undissociated nitrogen peroxide, an apparatus is described consisting of two bulbs of 50 and 100 c.c. capacity respectively connected together vertically through a glass stopcock, and closed above and below by similar means. The lower and larger bulb is filled with pure nitric oxide (2 vols.) and the upper with oxygen (1 vol.), both at atmospheric pressure. On opening the connecting tap, nitrogen peroxide is formed with a contraction in volume, the amount of which is determined by means of a mercury reservoir connected with the base of the lower bulb. From the volume occupied by the resulting gaseous product its degree of dissociation can be calculated.

A second apparatus is described to show the quantitative decomposition of certain gases for the purposes of demonstrating valence. It consists of a U-shaped eudiometer tube, one arm of which is closed by a stopper, through which passes a three-way tap and two iron or nickel rods, to which is attached inside a resistance spiral. The U-tube is charged with mercury, and the gas, hydrogen chloride, hydrogen sulphide, hydrogen phosphide, or methane which is being experimented with. The decomposition

is complete in the first three examples in less than a minute, methane requiring somewhat longer. The volume of residual hydrogen is read off after readjusting the pressure by means of the mercury. G. F. M.

An Improvement of Hofmann's Eudiometer. GAETANO MAGNANINI and A. VENTURI (*J. Amer. Chem. Soc.*, 1916, **38**, 1203).—A disadvantage of Hofmann's eudiometer is the liability of the stopcock to break when heated with steam. The authors therefore recommend that the stopcock should be replaced by a ground-glass stopper, tapering from below upwards. At the upper end of the stopper is a glass flange to prevent the stopper, when loosened, from falling down the eudiometer tube. In filling the eudiometer, the stopper is pushed down so that the flange rests on the top of the tube. The electrolytic gas is admitted through a side-tube, and after a short time the eudiometer is closed by pulling the stopper up. The outer tube is then adjusted, a current of steam passed through, and the experiment carried out in the usual way. E. G.

Inorganic Chemistry.

The Combining Volumes of Hydrogen and Oxygen. F. P. BURT and E. C. EDGAR (*Phil. Trans.*, 1916, [*A*], **216**, 393—427).—Although the values obtained by Scott and by Morley for the combining volumes of hydrogen and oxygen are nearly equal, it has been considered advisable to carry out a further series of measurements, because of the fact that the corrections which must be applied to Morley's data are somewhat uncertain. In order to eliminate errors due to uncertainty in the temperature and pressure coefficients, the gases, before combination, were measured at 0° and 760 mm., that is to say, under the conditions of the density determinations.

The experience of previous workers shows that the chief difficulty presented by the problem is the preparation of the two gases in a state of purity, and particular attention has been given to this point, the methods adopted for the ultimate purification of the gases being physical rather than chemical in nature.

The hydrogen obtained by electrolysis of an aqueous solution of barium hydroxide which had been recrystallised four times was purified by two different methods. In the one method, the dried gas was subjected to the action of cocoa-nut charcoal at the temperature of liquid air, and in the second the gas was made to pass through the walls of an electrically heated palladium tube. The oxygen was prepared either by electrolysis of aqueous barium hydroxide or by heating potassium permanganate, and was purified

by condensation and subsequent fractionation of the liquid oxygen.

The procedure adopted in determining the ratio of the combining volumes was to explode one volume of oxygen with rather more than two volumes of hydrogen, the volumes of the gases being measured consecutively in the same apparatus and to determine the volume of the residual hydrogen. By working with hydrogen in excess, the possibility of the formation of such substances as ozone, hydrogen peroxide, or oxide of mercury is diminished or eliminated.

Five series of experiments were made according to this method, and a sixth series in which the oxygen was taken in slight excess. Although no particular stress is laid on the results obtained by the last series of observations, it is claimed that they afford evidence that there is no constant error attaching to the employment of an excess of hydrogen. The final conclusion is that the volume ratio is represented with a high degree of probability by the figure 2·00288 at 0° and 760 mm. This differs from Scott's value by only 3 parts in 200,000.

By taking Morley's values for the density of hydrogen, 0·089873, and oxygen, 1·42900, this ratio gives 1·00772 for the atomic weight of hydrogen. More recent measurements of the density of oxygen have given the somewhat higher value of 1·42905, and in combination with the volume ratio this gives 1·00769 for the atomic weight of hydrogen. It is considered improbable that any further alteration in the density ratio will appreciably alter this value, and the authors draw the conclusion that the true value of the atomic weight of hydrogen lies very close to 1·0077. H. M. D.

The Thermal Decomposition of Hydrogen Peroxide in Aqueous Solution. WILLIAM CLAYTON (*Trans. Faraday Soc.*, 1916, **11**, 164—171).—Hydrogen peroxide does not volatilise appreciably from its aqueous solutions at 50—60°. The rate of decomposition is not affected by stirring. Traces of colloids greatly accelerate the decomposition. The most important factor is the purity of the water used as solvent, the tap-water employed giving a rate which is fifty times that of the best conductivity water. Either silica or wax-lined glass flasks may be used for the determinations.

C. H. D.

Solubility of Oxygen in Salt Solutions and in the Hydrates of these Salts. C. G. MACARTHUR (*J. Physical Chem.*, 1916, **20**, 495—502).—The solubility of oxygen in solutions of salts and sucrose of concentration varying between $N/16$ and $10N$, has been determined by the manganese hydroxide method at 25° for the following salts: Lithium chloride, sodium chloride, potassium chloride, rubidium chloride, cæsium chloride, sodium bromide, potassium bromide, potassium iodide, potassium nitrate, sodium sulphate, potassium sulphate, magnesium chloride, barium chloride, calcium chloride, and ammonium chloride. From the density of the solutions and the solubility of oxygen in them, the degree of

hydration of the above-mentioned salts is calculated. In all cases an increase in the concentration of the salt decreases the solubility of oxygen in a perfectly regular manner. Ammonium chloride has a very large effect on the solubility of oxygen; thus, for example, a *N*-solution of ammonium chloride dissolves only 0·07 c.c. of oxygen per litre. In the case of sucrose, it is shown that oxygen oxidises the sugar, and this interferes with the estimation of the amount dissolved. Potassium chloride, bromide, and sulphate and the chlorides of barium, calcium, and magnesium give hydration values which are approximately correct. The other salts give low values for highly ionised solutions, indicating that the particular ions increase the solubility of oxygen to a definite extent which is specific for that particular ion; or that it is the potential difference between the two ions present that causes this increase in oxygen solubility. J. F. S.

Reduction of Selenic Acid. W. Œchsner de Coninck and Chauvenet (*Ann. Chim. anal.*, 1916, **21**, 114).—A dark reddish-brown precipitate of selenium is obtained when selenic acid is boiled with the addition of formic, oxalic, malonic, or pyruvic acid; the precipitate is only slightly soluble, if at all, in carbon disulphide, and appears to be identical with that produced by the action of sulphur dioxide on selenic acid. The latter is not reduced by acetic or succinic acid. W. P. S.

The Synthesis of Ammonia. Zenghelis (*Compt. rend.*, 1916, **162**, 914—916).—Three series of experiments were made with the object of synthesising ammonia at low temperatures. In the first series, about 2200 c.c. of a mixture of hydrogen and nitrogen in the correct proportions were passed during ninety minutes through a tube containing 10 c.c. of water, or water acidified with sulphuric acid, heated at 90°, together with a metal to "atomise" the hydrogen. The metals used included platinum sponge, platinum black, and colloidal forms of platinum, palladium, silver, copper, mercury, and gold. In every case small quantities of ammonia were formed, colloidal silver in acidified water producing as much as 32·4 c.c. of *N*/100-solution of ammonia.

In the second series of experiments a current of hydrogen was passed through a solution evolving nitrogen by the decomposition of a mixture of sodium nitrite and ammonium chloride. Small quantities of ammonia were produced.

In the third series of experiments a metallic catalyst was added to the solution from which nitrogen was being produced, and the hydrogen was passed through as before. In these circumstances, both gases being in the atomic condition, more than 40% of the possible yield of ammonia was obtained when colloidal palladium was used, and 35% with colloidal platinum, these metals being prepared by Paals' method (A., 1904, ii, 180). E. H. R.

Electrolytic Preparation of Perborates. K. Arndt (*Zeitsch. Elektrochem.*, 1916, **22**, 63—64).—A solution of 40 grams of borax

and 120 grams of anhydrous sodium carbonate is electrolysed between a platinum gauze anode and a cathode made of tin tubing bent in a zigzag form round the anode. A current of water is circulated through the cathode, whereby the temperature is kept below 18°. A current of 20 amperes is used with an anode 8 × 6 cm. at 6 volts. After an hour the current is stopped and the solution cooled, when about 20 grams of sodium perborate separates out in small crystals. This is washed with a little ice-cold water and dried. A somewhat better yield can be obtained if 0·1 gram of sodium chromate and 1 drop of turkey-red oil are added to the solution. For the preparation of solutions of sodium perborate for bleaching purposes, it is recommended that the anode should be smeared with vaselin. In these circumstances, a yield of 27 grams per litre can be very efficiently obtained. J. F. S.

Extraction of Radium from Carnotite Ores with Concentrated Sulphuric Acid. HERMAN SCHLUNDT (*J. Physical Chem.*, 1916, **20**, 485—494).—Carnotite is boiled with concentrated sulphuric acid, whereby the radium and barium compounds present are converted into soluble hydrogen sulphates. The solution is filtered, and the radium obtained by dilution, when radium and barium sulphates are precipitated. Two types of carnotite ores are dealt with, a low grade ore containing 1·66% U_3O_8, 4·03% V_2O_5, and 4·88 parts of radium per billion, and a high grade ore containing 14·39% U_3O_8, 9·67% V_2O_5, and 42·78 parts of radium per billion. It is shown that by using sulphuric acid of more than 78%, at least 90% of the radium present in the ore may be recovered. A table of experimental data is appended to the paper, which shows the sources of loss of radium in the extraction, and compares the actual amount recovered with that actually present. J. F. S.

The Behaviour of Certain Metals towards Acids containing Hydrogen Peroxide. E. SALKOWSKI (*Chem. Zeit.*, 1916, **40**, 448—449).—Certain metals which are either insoluble or only soluble under other conditions in acids dissolve often in the cold and diluted acid, when hydrogen peroxide is present. With hydrochloric acid the action is due to the generation of free chlorine, and all metals except those which form insoluble chlorides are dissolved. Mercury is unacted on, however, and the formation of mercurous acetate when acetic acid and hydrogen peroxide are employed shows that oxidation to the bivalent condition is not possible under the conditions of the reaction. In dilute sulphuric acid containing hydrogen peroxide, copper, silver, mercury, nickel, and bismuth are soluble, whilst tin, lead, gold, platinum, and antimony are not attacked. Glacial acetic acid containing hydrogen peroxide attacks, even in the cold, copper, silver, lead, mercury, and bismuth, whilst on tin, nickel, gold, and platinum it remains without action. It is suggested that hydrogen peroxide, in conjunction with an acid, should find a wider application in analysis for the solution of metals and alloys. G. F. M.

Densities of Alkali Metal Amalgams and Mercury. James R. Withrow (*J. Physical Chem.*, 1916, **20**, 528—531).—Polemical; calling attention to the fact that sodium, potassium, and lithium amalgams are lighter than mercury, and not heavier, as is suggested in a diagram by Kerp (A., 1898, ii, 516), who depicts and labels solid potassium amalgam as settling below metallic mercury and dilute amalgam. This error is also copied into Abegg's Handbuch. A list of specific volumes of alkali amalgams is quoted from Maey (A., 1899, ii, 547). J. F. S.

Unusual Explosion in Connexion with Potassium Chlorate. Floyd E. Rowland (*J. Ind. Eng. Chem.*, 1916, **8**, 517—518).—A pestle and mortar had been used for powdering potassium chlorate, and had then been washed and dried. A few days later the same pestle and mortar were used to crush some pumice stone, when explosion occurred, the pestle and mortar being shattered. The wooden handle of the pestle had been sealed into the ball with sulphur, and a small amount of the chlorate had evidently worked into the crevice, come into contact with the sulphur, and thus caused the explosion. W. P. S.

The Solubility of Sodium Hydroxide in Liquid Ammonia. Michel Skossarewsky and Nicolas Tchitchinazé (*J. Chim. phys.*, 1916, **14**, 153—175).—According to measurements of the solubility of sodium hydroxide in pure liquid ammonia which were made by the direct method and by the conductivity method, the saturated solution contains only about 2·5 mg. per 1000 grams of solvent, or 1·8 mg. per litre. Traces of water have a considerable influence on the solubility of the hydroxide. H. M. D.

The Allotropy of the Ammonium Haloids. II. F. E. C. Scheffer (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1498—1513. Compare this vol., ii, 31).—It has been shown previously that there are two enantiotropic forms of ammonium chloride with a transition temperature at 184·5°. The heat change involved in this transformation has been determined by calorimetric experiments, in which weighed quantities of ammonium chloride heated to accurately measured temperatures above and below the transition point were introduced into the calorimeter and dissolved in the contained water. From the data thus obtained, the heat of transformation of the α- into the β-form is calculated to be -1030 cal.

The existence of enantiotropic forms of ammonium chloride is of particular interest in view of the fact that Wegscheider (A., 1909, ii, 23) has suggested that the difference in the vapours of dry and of moist ammonium chloride may be due to the existence of polymorphic forms, the one being transformed into the other under the catalytic influence of water vapour. The available data are examined in reference to this hypothesis, and the author arrives at the conclusion that it is untenable. The desirability of further experiments on the vapour pressures of dry ammonium chloride is emphasised. H. M. D.

Causes of Error Affecting Determinations of Atomic Weights. V. Gaseous Impurities contained in Silver with Reference to its Use as an Auxiliary Atomic Weight Standard. PH. A. GUYE and F. E. E. GERMANN (*J. Chim. phys.*, 1916, **14**, 204—243). —In view of the important position which silver occupies in connexion with the determination of the atomic weights of the elements, the authors consider that recent measurements of its atomic weight are not sufficiently concordant and that some hitherto unsuspected source of error is responsible for the discrepancies between the several values obtained in different series of experiments.

The assumption that the lack of agreement is partly due to the presence of gaseous impurities in metallic silver is found to receive considerable support from experiments in which the authors have investigated the small quantities of gas which are retained by the metal after it has been fused in an atmosphere of hydrogen, the gas being bubbled through the molten metal. Although the amount of hydrogen retained by the metal after this treatment is negligibly small, it is found that certain other gases, notably carbon monoxide, may be retained in quantities sufficient to account for appreciable variations in the experimentally determined atomic weight. The gas was liberated by converting the metallic silver into silver iodide by the action of gas-free iodine and analysing the gas by means of the apparatus described by the authors (this vol., ii, 445). Other experiments show that the gaseous impurity is not uniformly distributed throughout the metal, the gas content varying according to whether peripheral or central portions of the metal are examined.

The quantities of gas found in the samples of silver with which the experiments have been made are shown to be of sufficient magnitude to account for appreciable variations in the determination of the atomic weight of silver. H. M. D.

Metallic Calcium and its Use in Gas Analysis. A. SIEVERTS (*Zeitsch. Elektrochem.*, 1916, **22**, 15—18).—It is shown that metallic calcium exists in an active and an inactive form as far as its power of absorbing gases is concerned. Active calcium commences to absorb nitrogen at 300°, and has a maximum action at 440°; as the temperature is further increased the rate of combination slowly decreases until at 800° it has ceased. The velocity of absorption is dependent on the presence of a layer of nitride, and is only brought to its maximum value after such a layer has been formed. The velocity of nitride formation is expressed by $v=kp^{4/3}$, in which v is the velocity, p the nitrogen pressure, and k a constant. The inactive form of calcium only commences to combine with nitrogen at 800°. The difference between the two forms is not due to the existence of allotropes, but rather to the state of subdivision. The active variety is prepared by slowly cooling molten calcium. This variety produces calcium nitride, which is brown in colour. The non-active form is produced by suddenly cooling calcium from 840°; this variety produces a black

nitride. Active calcium absorbs hydrogen between 150° and 300° and above 600°. Calcium nitride absorbs hydrogen, carbon monoxide, carbon dioxide, and methane. These properties of calcium make it extremely useful for the estimation of the inactive constituents of the atmosphere. Details of the experimental methods of effecting this estimation are indicated in the paper. J. F. S.

The Maximum Solubility of Calcium Sulphate. HENRY LE CHATELIER (*Compt. rend.*, 1916, **162**, 931—932).—Polemical. A reply to Colson (*Compt. rend.*, 1916, **162**, 753). W. G.

The Several Forms of Calcium Carbonate. JOHN JOHNSTONE, H. E. MERWIN, and E. D. WILLIAMSON (*Amer. J. Sci.*, 1916, [iv], **41**, 473—512).—A critical résumé of the known facts concerning the several forms of calcium carbonate, of the methods available for obtaining and identifying them, and of their physical properties and stability relations. Besides the two well-known forms, calcite and aragonite, a third crystalline form has been identified by the authors, and is referred to as $\mu CaCO_3$. This form was obtained best by precipitation at 60°, but was always contaminated with calcite or aragonite, from which it could be separated by flotation in a liquid D 2·6. It has D 2·54, those of calcite and aragonite being respectively D 2·71 and D 2·88. It forms microscopic plates belonging to the hexagonal system. Uniaxial positive interference figures were observed, and the refractive indices were determined, 1·550 and 1·650 within about ±0·005. Other reputed forms of calcium carbonate are either identical with one or other of the above three forms, or, as in the cases of "vaterite" and "amorphous" $CaCO_3$, are not definite forms, their divergent properties being due to differences in size of grain and mode of aggregation.

Of the three forms, calcite is the stable one, at ordinary pressures, between 0° and 970°, above which temperature it inverts irreversibly to α-$CaCO_3$. Aragonite and μ-$CaCO_3$ are always unstable towards calcite, and their conditions of stability have not been determined, although there is some indication that aragonite has a stable field of existence below −100°. Aragonite does not change into calcite at an appreciable rate below 400°; μ-$CaCO_3$ persists indefinitely at the ordinary temperature when dry, but when heated goes over into calcite.

Calcium carbonate hexahydrate is precipitated in alkaline solution at 0°. It forms microscopic but well-formed, colourless, monoclinic crystals. The only forms observed were the prism and the three pinacoids: $a:b:c=1·02:1:?$; $2E=72°\pm3°$. The refractive indices are: $\alpha=1·460$, $\beta=1·535$, $\gamma=1·545$.

The natural occurrence of the different forms of calcium carbonate is discussed, with special reference to the production under natural conditions of the unstable form, aragonite.

E. H. R.

The Zinc-Copper Couple Hypothesis of Brass Corrosion. ARNOLD PHILIP (*Trans. Faraday Soc.*, 1916, **11**, 244—257).—Both

the α and the β phases of brass are solid solutions, and may be regarded as consisting of minute particles of copper and zinc in juxtaposition, and on this view the corrosion of brass is regarded as due to the electrolytic action between such local couples. The effect of an external difference of potential on such an arrangement of small couples is shown by diagrams and formulæ. Experiments are being made to determine the effect of varying this external difference of potential. C. H. D.

The Corrosion of a Solid Solution—70 : 30 Brass. W. E. Gibbs (*Trans. Faraday Soc.*, 1916, **11**, 258—266).—The rate of corrosion of copper in sea-water is diminished by alloying with zinc until the alloy corresponding with the formula CuZn is unattacked by sea-water at the ordinary temperature. There is a secondary minimum at 70% Cu, but this disappears after the corrosion has proceeded for a few weeks.

The initial rate of corrosion of 70:30 brass increases with rising temperature up to 50° and then rapidly diminishes. The diminution with time is more rapid at high temperatures than at low. At first the attack is chiefly on the copper, then it becomes general, and finally zinc is increasingly dissolved in preference to copper. Pure copper dissolves readily in sea-water at first, but the action is then interrupted, probably by the formation of a film. Zinc is soon covered by a film of carbonate. The influence of aeration and concentration of the sea-water is also considered.

Hard-drawn brass corrodes less rapidly than the annealed alloy, but there is a larger proportion of zinc in the corrosion product. Attached particles may act electrolytically or may serve for the accumulation of oxychlorides. C. H. D.

Egyptian Blue. Laurenz Bock (*Zeitsch. angew. Chem.*, 1916, **29**, i, 228).—The author claims priority for the French ultramarine works of Deschamps Frères for the reproduction of Egyptian-blue (compare Laurie, McLintock, and Miles, A., 1914, ii, 128). It was prepared by fusion in an ultramarine furnace of quartz (50 parts), chalk (21 parts), copper oxide (24·4 parts), and sodium carbonate (4·6 parts), all in the finest powder and completely free from iron. The product, washed with hydrochloric acid and hot water, had the composition $CaO,CuO,4SiO_2$, and corresponded in its chemical and physical properties completely with the material used by the ancients. G. F. M.

Separation of Erbium from Yttrium. I. P. S. Willand and C. James (*J. Amer. Chem. Soc.*, 1916, **38**, 1198—1202).—In carrying out a systematic investigation of the separation of erbium from yttrium, it was considered desirable to start with two types of oxide material, one containing an excess of yttrium and the other consisting chiefly of erbium. In the present paper an account is given of experiments with material of the former type.

The methods of separation tested were fractional precipitation with sodium phosphate, potassium ferrocyanide, sodium nitrite,

potassium cobalticyanide, sodium carbonate in presence of ammonium acetate, ammonium oxalate in presence of ammonium acetate, ammonium succinate in presence of ammonium acetate, sodium phosphate in presence of ammonium acetate, and sodium hydroxide in presence of excess of tartaric acid; fractional crystallisation of the double ammonium sulphates, the diphenylsulphonates, and the picrates; and fractional precipitation from acetone solution by means of tartaric acid and malonic acid.

The best results were obtained by the nitrite, cobalticyanide, and phosphate methods. Fractional precipitation with sodium nitrite is recommended for work on a large scale on account of the cheapness of the salt and the ease of manipulation. E. G.

Action of Nitric Acid on Aluminium. R. SELIGMAN and P. WILLIAMS (*J. Soc. Chem. Ind.*, 1916, **35**, 665—672).—Experiments are described on the rate of dissolution of aluminium in nitric acid under varying conditions. It was found that the most important condition affecting the rate of dissolution is temperature, an increase of 10° over a considerable temperature range being sufficient to increase the dissolution by 100%; the life of aluminium vessels used for storage or transport of nitric acid can therefore be greatly prolonged by keeping the temperature as low as possible. The concentration of the acid is also an important factor, the most active solvents being acids containing 20—40% by volume of nitric acid (D 1·42). On the other hand, acids containing 94·7% HNO_3 were extremely inactive, a rate of dissolution of only 0·015 mg. of aluminium per 100 sq. cm. per twenty-four hours being observed. The presence of chlorine up to 0·05% in the acid did not affect the rate of attack, but 0·04% of sulphuric acid raised the rate of dissolution from 36 to 62 mg. per 100 sq. cm. per twenty-four hours. The presence of lower oxides of nitrogen also accelerates dissolution. The amorphous metal is more readily attacked than the crystalline, but the presence of impurities in the metal is of less influence than has hitherto been assumed. Mixed nitric and sulphuric acids attack the metal much more readily than pure nitric acid, and statements to the contrary are erroneous. No local action or pitting was observed as the result of attack by nitric acid on aluminium sheet of high quality; the action was quite uniform. The influence of annealing aluminium on its resistance towards nitric acid is at present not clear. Exposure for a few hours at 100—125° seemed to increase its resistance, but by a longer exposure to the same temperature the metal lost its comparative immunity from attack. Also metal freshly annealed at 540° is more resistant than metal which has stood for ten days after annealing. The existence of a number of hydrates of aluminium nitrate is recorded (T., 1916, **109**, 612). G. F. M.

Aluminium-Zinc Alloys. O. BAUER and O. VOGEL (*Chem. Zentr.*, 1916, i, 551—552; *Mitt. K. Mat. Prüfungsamt*, **33**, 146—198).—After a critical discussion of the previous work on

these alloys, particularly that of Rosenhain and Archbutt (A., 1911, ii, 895), further thermal and microscopic investigations in completion of the work of these authors is described. Additional experiments on aluminium foil and aluminium-zinc alloys containing 7—10% of zinc, and consisting of γ-mixed crystals, were made. The presence of zinc in a sample is rapidly made evident by etching with 5% sodium hydroxide, the surface of aluminium remaining white, whilst the mixed crystals become covered with a deep black, superficial layer, which is not removed by washing with water and cotton-wool (distinction from copper). Investigation of the action of water on these alloys in respect to annealing showed that the action alters according to the temperature. Aluminium foil annealed at 400° was most resistant, whilst the alloy containing 8·73% zinc was least attacked when it has been annealed between 400° and 500°, and most attacked when annealed at 200°. Whilst zinc-free aluminium, either annealed or unannealed, developed no superficial roughnesses or spots under the influence of the atmosphere, the alloys became covered with white spots, which after removal left a distinctly rough surface. As a protection against the action of water, two to four hours' treatment at 90—95° in a bath containing 2·5% K_2CO_3, 2·5% $NaHCO_3$, and 1% $KHCrO_4$ in aqueous solution is recommended. The metal is covered thereby by an iridescent, deep grey film. G. F. M.

Formation of Aluminium Nitride from Alumina, Carbon, and Nitrogen. II. W. FRANKEL and J. SILBERMANN (*Zeitsch. Elektrochem.*, 1916, **22**, 107—109. Compare A., 1913, ii, 509).—A continuation of the previous work. The present paper deals with the influence of various sorts of carbon on the reaction. The following varieties of carbon have been used: acetylene carbon, powder petrol coke, graphite, and wood charcoal, both purified and unpurified. In the case of petrol coke and graphite, it is shown that the reaction takes place more slowly than with acetylene carbon. In the case of wood charcoal, it is shown that the unpurified material gave a much higher reaction velocity than acetylene carbon, whereas the material purified by heating in chlorine and extracting with water and hydrochloric acid gave a value of the same order as that of acetylene carbon. The increased velocity in the case of unpurified wood charcoal is attributed to the presence of alkali in this material, since it has previously been shown that alkali has a powerful accelerating influence on the rate of formation of aluminium nitride. In an addendum to the paper, Askenasy compares the efficiency of the nitride production from pure alumina and pure carbon with that from bauxite and coke. The results are much to the advantage of the impure materials. In the case of pure material about 11·5% of nitrogen is fixed, whilst in the latter the material contains about 23·5% of nitrogen. J. F. S.

Hydrates of Aluminium Nitrate. RICHARD SELIGMAN and PERCY WILLIAMS (*J. Chem. Soc.*, T., 1916, **109**, 612—617).—During the course of experiments on the action of nitric acid on

aluminium, three distinct hydrates of aluminium nitrate have been found to exist. Saturated solutions of the nitrate prepared by heating the metal with nitric acid (D 1·42) and filtering through glass-wool deposit the hydrate, $Al_2(NO_3)_6,12H_2O$, sometimes in the form of single crystals weighing several grams if cooling is slow. In acid of the above strength this hydrate is unstable, and is readily transformed by inoculation into the stable hydrate, $Al_2(NO_3)_6,18H_2O$. In acid of D 1·50 at 20° the hydrate containing $12H_2O$ is alone stable.

The hydrate with $12H_2O$ is much more soluble in nitric acid (D 1·42) than that with $18H_2O$.

The third hydrate, which has been obtained in the form of very thin plates, is very unstable when separated from the mother liquor. It appears to contain $15H_2O$ or $16H_2O$, and to be stable in acid of density between 1·42 and 1·50. E. H. R.

The Devitrification of Crystal [Glass free from Lime]. HENRY LE CHATELIER (*Compt. rend.*, 1916, **162**, 853—855).—Observations on the effect of lowering the temperature of the furnace on the physical structure of the glass being made. Two samples of glass were examined, namely: (1) normal crystal, used for making articles *de luxe*; (2) a variety called "quinquet," used for making lamps; the base of the former consisting mainly of potash and of the latter of soda. The temperature of the furnaces, owing to fighting in the district, had to be lowered from 1350° to 800° for twenty days, and then the fires had to be put out. On breaking the crucibles, devitrification was only noticeable in the second variety, felted masses of very thin, hexagonal plates being seen at the bottom of the crucible. The vitreous mass was transparent at the top, but held in suspension small, isolated plates and other more voluminous crystals, grouped together in such a way as to give more or less regular spherolites. These crystals consist of silica in the form of tridymite. W. G.

Titration with Permanganate in Strongly Alkaline Solution. BOHUSLAV BRAUNER (*Zeitsch. anal. Chem.*, 1916, **55**, 225—267).—Arsenious acid reduces permanganate in alkaline solution to Mn_2O_3 if an electrolyte, such as potassium sulphate, is present in the solution to cause precipitation of the colloidal $Mn(OH)_3$; in the absence of an electrolyte, the hydroxide remains in colloidal solution and the reduction proceeds to MnO_2. Thallous salts are completely oxidised to thallic salts by permanganate in alkaline solution; cerous salts are oxidised to the CeO_2 state. Lead yields an oxide which contains rather more oxygen than corresponds with the compound $PbO + PbO_2$. Selenious acid and tellurous acid are oxidised completely, as is also ferrous iron. In slightly alkaline solution, nickel yields an oxide of the formula $Ni_{10}O_{11}$; in strongly alkaline solution, the oxidation proceeds approximately to the formation of Ni_2O_3. Cobalt yields an oxide containing somewhat more oxygen than corresponds with Co_2O_3. W. P. S.

The Transformations of Pure Iron. SIR ROBERT HADFIELD (*Trans. Faraday Soc.*, 1916, **11**, 125—128).—An introduction to a general discussion. The explanation of the changes in the properties of iron with temperature on the basis of allotropy has broken down, and the most promising line of investigation is now the study of the nature of the carbides contained in steels of different kinds. C. H. D.

The Transformations of Pure Iron. A. E. OXLEY (*Trans. Faraday Soc.*, 1916, **11**, 129—134).—The A_3 point in iron is not to be regarded as an allotropic change point. A true allotropic change, such as that of oxygen into ozone or of white into red phosphorus, is accompanied by a development or absorption of energy which is of a different order from that involved in the fusion of solid elements, whilst the thermal change in the recalescence of iron is even smaller than the heat of fusion of a metal. The so-called allotropic changes of iron are rather to be regarded as changes in the grouping of the atoms in the crystal, and are closely associated with the variations in the magnetic properties. Thus, cooling through A_3 may be accompanied by closer grouping of the molecules in the direction of spontaneous magnetisation, there being no change in the crystalline symmetry. There is a thermal effect corresponding with the difference of the potential energies above and below the change point. C. H. D.

The Allotropy of Iron. F. C. THOMPSON (*Trans. Faraday Soc.*, 1916, **11**, 134—140).—The changes in the properties of iron with temperature indicate the existence of four allotropic modifications, α, β, γ, and δ. The transformation points are at 768°, 900°, and 1400° respectively, whilst a slight change may be detected by thermal and dilatometric measurements at 830°. The A_3 point is of the same nature as the other critical or transformation points. There is evidence from magnetic observations that the molecular weight of solid iron in its different modifications is different, β-iron being probably Fe_3, γ-iron Fe_2, and δ-iron Fe. These modifications must have different types of packing in the crystal, although having the same crystal system. The changes are of exactly the same kind as those which are recognised to be allotropic in zinc and sulphur. C. H. D.

The Corrosion of Steel Alloys. SIR ROBERT HADFIELD (*Trans Faraday Soc.*, 1916, **11**, 183—197).—The presence of nickel in steel does not greatly retard corrosion unless in large proportions. Of the alloys of iron and chromium prepared by the author in 1892, those containing about 11% of chromium and 1% of carbon are found to have remained bright and free from rust, although the resistance to dilute sulphuric acid is not high. The 'stainless steel' used for cutlery is similar in composition, containing 10—12% of chromium, but only 0·3—0·4% of carbon.

Curves are given showing the influence of varying proportions of silicon, chromium, nickel, and tungsten on the resistance of steel to attack by 20% sulphuric acid. C. H. D.

Physical and Mechanical Factors in Corrosion. CECIL H. DESCH (*Trans. Faraday Soc.*, 1916, **11**, 198—203. Compare A., 1915, ii, 346).—The difference between the results of tests made by immersing metals and alloys in acids and determining the loss of weight, and actual experience of atmospheric or other forms of corrosion, is largely due to differences in the physical and mechanical properties of the corrosion product. A tough, adherent product acts as a protection against further action, whilst a loose, porous product allows the entrance of the electrolyte and frequently, as in the case of iron rust, accelerates corrosion by its electronegative character. The manner in which corrosion begins is determined by the chemical or mechanical heterogeneity of the metal. Comparative experiments on corrosion should always include a microscopical study of the process, especially in its initial stages. C. H. D.

The Relative Corrodibilities of Iron and Steel. J. NEWTON FRIEND (*Trans. Faraday Soc.*, 1916, **11**, 204—211).—Iron immersed in tap-water yields a rust consisting almost entirely of ferric oxide, and there is no pitting, but if made alternately wet and dry, pitting takes place, and both ferric and ferrous oxides are found in the rust. If only partly immersed, severe local corrosion takes place, with the formation of much ferrous oxide. Concentrated solutions of alkali nitrates yield a bright green rust. Slightly alkaline solutions of mineral salts produce pitting, even when the iron is in the form of Kahlbaum's electrolytic foil.

The relative resistance of different varieties of iron and steel towards different corroding media varies so widely that no general statement can be made as to the resisting power unless the conditions to which the metal is to be exposed are specified. Consequently, in the present state of knowledge the final appeal must be made to experiments on a large scale under working conditions. It cannot be said that either wrought iron or steel has an absolute advantage over the other material in regard to resistance to corrosion. C. H. D.

The Influence of Composition on the Corrosion of Steel. LESLIE AITCHISON (*Trans. Faraday Soc.*, 1916, **11**, 212—234).—The loss of weight of annealed carbon steels in 3% sodium chloride solution passes through a minimum at 0·45% C, and then rises to a maximum at 0·9%. In 10% sulphuric acid the result is similar, whilst 1% sulphuric acid shows the maximum, but not the minimum. In the tungsten series there is a maximum corrosion at 21% W. This is the composition at which the excess carbide reaches a maximum. Vanadium steels are readily corrodible, a maximum occurring at from 6 to 10% V, according to the solvent. Chromium diminishes the amount of corrosion, which becomes zero in sodium chloride or dilute acid at 19% Cr, although steel of this composition is attacked to a remarkable extent by the stronger acid. Addition of cobalt steadily diminishes the liability to corrosion. Copper increases the corrosion in sodium chloride or 1% sulphuric

acid, but quantities of 1% or more diminish the corrosion in 10% sulphuric acid, owing to the formation of a protective layer of copper after the initial stage.

The results are less regular when the steels are immersed in tap-water in the dark, but are more similar to those obtained in 1% sulphuric acid than either of the other series. The presence of copper accelerates the corrosion.

Homogeneous structure is not in itself a safeguard against corrosion, and it appears that the determining factor is the composition of the solid solution. Carbides are usually unattacked, and accelerate corrosion by acting as cathodes. C. H. D.

The Corrosion of Iron and Steel. S. WHYTE (*Trans. Faraday Soc.*, 1916, **11**, 235—236).—In a case of rapid corrosion of a mild steel water-pipe embedded in earth, it was found that the steel had been overheated, and had a coarse, angular arrangement of the ferrite. Laboratory tests show that such an overheated steel is corroded 20% more rapidly than the same steel in the normalised condition. When an applied electromotive force is employed, the ferrite is first attacked, and the action then extends to the pearlite (compare Desch and Whyte, A., 1914, ii, 660). C. H. D.

The Position of Martensite in the Iron–Carbon Diagram. WITOLD BRONIEWSKI (*Compt. rend.*, 1916, **162**, 917—919).—The stability of any substance at a given temperature being dependent on its free energy, an attempt has been made to determine the position of martensite in the iron–carbon system by determining its *E.M.F.* of solution. A normal solution of ferrous sulphate was used as the electrolyte, and the *E.M.F.* given respectively by annealed and quenched steels containing from 0·07 to 1·12% of carbon were compared, first against an anode of graphitised carbon, secondly against a cathode of very mild steel.

It was found that the *E.M.F.* obtained with martensite was lower than that given by the active element in annealed steel, namely, ferrite, indicating that the solution of carbon in ferrite to form martensite diminishes the free energy. The definition of martensite given by Le Chatelier, as a solution of carbon in α-iron, is confirmed. It probably becomes stable towards the temperature of liquid air, and its formation by quenching is in accordance with the Bancroft-Ostwald law that the form which first appears is not the most stable, which would be austenite, but the one closest to this. In the diagram the martensite area appears as a very narrow band on the left-hand side, extending rapidly at very low temperatures with increasing carbon content. E. H. R.

Dissociation of Ferric Oxide in Air. J. C. HOSTETTER and R. B. SOSMAN (*J. Amer. Chem. Soc.*, 1916, **38**, 1188—1198).—In an earlier paper (this vol., ii, 331) it was shown that ferric oxide, Fe_2O_3, dissociates to form a continuous series of solid solutions from Fe_2O_3 to very near Fe_3O_4, and that the curve obtained by plotting the dissociation pressures against the composition at a given temperature rises rapidly as the composition approaches pure Fe_2O_3.

Further experiments have now been carried out which show that there is a measurable dissociation of ferric oxide in air at all temperatures between 1100° and 1300°, and that the amount of dissociation increases with the temperature. This was demonstrated by determining the differences in the weight of ferric oxide when ignited in air and in oxygen; it was found that as the temperature was increased the difference in weight was also increased.

It was observed that platinum lost weight when heated in contact with ferric oxide at 1100—1200°, whilst alundum was not affected appreciably at these temperatures; an alundum boat was therefore used in the experiments. E. G.

Chrome Yellow. I. The System $PbSO_4 + K_2CrO_4 \rightleftarrows PbCrO_4 + K_2SO_4$. JAROSLAV MILBAUER and KAMIL KOHN (*Zeitsch. physikal. Chem.*, 1916, **91**, 410—430).—With the object of explaining the formation and nature of the variously tinted forms of chrome-yellow prepared on the large scale, the authors have investigated the reaction $PbSO_4 + K_2CrO_4 \rightleftarrows PbCrO_4 + K_2SO_4$ from the point of view of the phase rule and of chemical equilibrium. It is shown that the reaction proceeds practically completely in the direction from left to right, and at such a rate that it can be readily followed. The velocity in the opposite direction is very small, and can only be detected by the great sensitiveness of the reaction, $CrO_4'' + 8H^{\cdot} + 6I' = Cr^{\cdot\cdot\cdot} + 4H_2O + 3I_2$. From determinations of the stability, it is shown that the solid phase $PbSO_4$ cannot exist in the presence of K_2CrO_4, K_2SO_4, and $PbCrO_4$, and, further, the existence of double salts is unlikely. The determination of the mass-action curve was rendered very difficult owing to the very small equilibrium constant and the strong adsorption. Adsorption is very marked at lower temperatures and high concentration, and is doubtless of importance in the manufacture of particular shades of chrome-yellow. The equilibrium constant is so small that it follows that the region of existence of lead sulphate practically vanishes from the isothermal diagram. The velocity of the reaction increases with increasing temperature, but here also the adsorption causes the velocity coefficients to appear as functions of the adsorption. It follows as a general result that the manufacture of chrome yellow can be carried out from lead sulphate, and that various shades can be obtained by varying the conditions, temperature, concentration, and time. It also follows that in the manufacture an excess of lead acetate should be used, for this will secure the absence of potassium chromate in the product. This point is essential, since such chromate would rapidly convert the lead sulphate which is necessary for the particular shade into lead chromate, and so the shade would be changed. The theory which explains the stability of chrome-yellow by the existence of a lead sulphochromate is unlikely, since the present experiments make the existence of these double salts extremely doubtful. J. F. S.

Double Refraction of Vanadium Pentoxide Sol. H. FREUNDLICH (*Zeitsch. Elektrochem.*, 1916, **22**, 27—33).—It is shown that a solution of vanadium pentoxide sol when stirred exhibits yellow, shining streaks, as though it contained fine crystals floating in it. If a similar solution is examined by transmitted light, it is seen to be quite clear, and dark streaks are observed. These facts are due to double refraction, which is set up when the sol is stirred. It is shown that when examined under crossed nicols the sol exhibits all the properties of a doubly refracting substance. In addition to stirring, the same phenomena can be brought about by placing the sol in a magnetic or an electric field. When examined ultramicroscopically, the sol is seen to contain particles elongated along one axis, and it is to these particles and their arrangement that the double refraction is attributed. The connexion between the present case and the Majorana phenomenon and that of liquid crystals is discussed.

J. F. S.

The Presence of Nickel in Native Platinum. S. PIÑA DE RUBIES (*Arch. Sci. phys. nat.*, 1916, [iv], **41**, 475—478).—The author has submitted a large number of samples of native platinum from different deposits to spectrochemical examination, and finds that in every case nickel is present in weighable quantity. Platinum ores rich in iron give the most intense nickel spectrum, but so far no direct relationship has been found between the iron and nickel contents. W. G.

Volatilisation of Platinum. G. K. BURGESS and R. G. WALTENBERG (*J. Ind. Eng. Chem.*, 1916, **8**, 487—490; *J. Washington Acad. Sci.*, 1916, **6**, 365—366. Compare A., 1915, ii, 586).—Platinum ware in the form of crucibles, of whatever degree of purity, behaves, as regards loss or gain of weight when heated in air, in a manner characteristic only of the temperature of heating. Each impurity (such as iridium, rhodium, or iron) exerts an independent effect on the volatilisation, but the loss is not appreciable below 900°. There may even be a slight gain in weight when impure platinum is heated below 900°, owing to the iron diffusing to the surface and oxidising. At higher temperatures, iron and rhodium decrease the volatilisation, whilst iridium increases it, the loss in weight increasing with the iridium content and the temperature. In an oxidising atmosphere at about 1000°, platinum, in the presence of (but not in contact with) silica, apparently takes up small quantities of this substance. The loss in weight due to the solution of substances in hydrochloric acid, after heating, is variable, depending on the crucible; this loss is relatively greater at low than at high temperatures. The losses caused by heating, acid treatment, and iron diffusion continue after the first treatment, although, of course, the concentration of iron must diminish. There appears to be no platinum made which does not contain some iron. W. P. S.

Ruthenium Dicarbonyl. ROBERT MOND (*Rep. Brit. Assoc.*, 1915 393).—Ruthenium dicarbonyl has been obtained by heating finely powdered ruthenium in carbon monoxide at 300° under a pressure of 400 atmospheres. It is extracted from the residue by solution in alcohol. Unlike other carbonyls, it is not volatile.

C. H. D.

Mineralogical Chemistry.

Composition of Apatites. FERRUCCIO ZAMBONINI (*Compt. rend.*, 1916, **162**, 919—921).—By fusing tricalcium phosphate with calcium chloride, crystals of an apatite are obtained having the composition $3Ca_3(PO_4)_2,CaCl_2$, but by using sodium chloride instead of calcium chloride, the author has obtained well-formed crystals, very small and transparent, corresponding with the formula $4{\cdot}34Ca_3(PO_4)_2,CaCl_2$. These contain some sodium, but the interesting point about them is their low chlorine content. The generally accepted formula for the apatite group is

$$3Ca_3(PO_4)_2,Ca[O,(OH)_2,Cl_2,F_2,CO_3],$$

but it is now evident that the characteristic double salt can form solid solutions with at least one of its constituents. Numerous instances of natural apatites containing more than 3 molecules of tricalcium phosphate are adduced, and frequently these contain an inexplicable excess of CaO which cannot be attributed to analytical error. E. H. R.

Xanthophyllite in Crystalline Limestone. ARTHUR S. EAKLE (*J. Washington Acad. Sci.*, 1916, **6**, 332—335).—This mineral, and its green variety waluewite, has previously been found only in the Slatoust district, Urals, where it occurs in schistose rocks. It is now recorded in crystalline limestone from Crestmore, near Riverside, in California, where it occurs with monticellite and wilkeite (A., 1914, ii, 283) embedded in sky-blue, coarsely crystalline calcite. The waluewite forms six-sided plates of a deep grass-green colour. The optic axial plane is parallel with the ortho-pinacoid (100), axial angle (Na) $= 12—18°$, negative, $\beta = \gamma = 1{\cdot}660$; analysis I. The monticellite is pale brown with a somewhat greasy lustre; it occurs as small masses and grains scattered through the calcite, but occasionally as wide bands of massive material; analysis II.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Ign.	Total.	Sp. gr.
I.	16·74	42·70	2·85	0·41	13·09	20·03	4·49	100·31	3·081
II.	36·02	—	—	2·82	34·36	24·74	1·25	99·19	—

These minerals are the product of hydrothermal metamorphism of the limestone. The composition of the waluewite can be expressed as a mixture of monticellite + olivine + spinel + diaspore in the proportions 6 : 1 : 5 : 6. L. J. S.

Cyclopite of Santa Maria la Scala (near Acireale). S. Di Franco (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 693—697).—The cyclopite of Santa Maria la Scala occurs in shining plates as much as 2 mm. in length along the greater diagonal, mostly almost white and transparent, but sometimes coloured yellow or red by oxides of iron, $a:b:c=0.63473:1:0.55007$, D 2·721, the high specific gravity being due to inclusions, especially of magnetite; simple crystals are rare. The composition is:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	Loss at red heat.	Total.
43·10	30·12	1·80	0·95	19·50	0·52	2·18	1·25	0·92	100·34

The fact that crystals of aragonite are found implanted on the faces of the lamellæ of cyclopite indicates the latter to be older than the former. T. H. P.

Gas Content of the Taunus Rocks and its Relationship to the Gases of the Wiesbaden Thermal Springs. F. Henrich (*Zeitsch. Elektrochem.*, 1916, **22**, 64—69).—An account is given of previous work done in connexion with the composition of the dissolved solids and gases of the Wiesbaden hot springs, together with theories propounded to account for these springs. The present paper deals with the analysis of the gases obtained from the various strata of the Taunus range and the connexion between the composition of these gases and those collected from the springs. The material was obtained from borings, and was intimately mixed with sodium pyrosulphate and heated. The gases evolved were collected and analysed. Fifteen grams of material yielded the following volumes of gas: mica, 5·6—8·2; shale, 10·0; violet slate, 10·4; black slate, 6·5; green slate, 4·7; quartzite, 3·4; quartz, 2·5, and basalt, 2·7. The gases from the rocks contained nitrogen, oxygen, carbon dioxide, argon, helium, and hydrocarbons. The amount of inactive gases is in such a proportion that it cannot possibly be derived from the air. The ratio of the various constituents points to the view that whilst a considerable quantity of the gases evolved in the springs comes from the Taunus rocks, a great deal of the nitrogen and argon must be derived from the rocks which are still deeper in the earth. J. F. S.

Analytical Chemistry.

Use of Titanium Trichloride in Volumetric Analysis. A. MONNIER (*Ann. Chim. anal.*, 1916, **21**, 109—113).—Ferric chloride in hot hydrochloric acid solution may be titrated with titanium trichloride solution if a few drops of dilute methylene-blue solution are added to serve as the indicator. Chromates may be

titrated similarly. In the case of cupric salts, safranine or induline must be used as the indicator, since methylene-blue is reduced by the titanium trichloride before the cupric salt is attacked. Titanium trichloride solution is also useful for the estimation of titanium in ores; the sample is fused with potassium hydrogen sulphate or sodium peroxide, the mass then dissolved in hydrochloric acid, the solution reduced with powdered zinc, filtered, and the filtrate treated with an excess of standard ferric chloride solution, the excess of the latter being then titrated as described with titanium trichloride solution. Copper and iron in the same solution may be estimated by first titrating a portion of the solution with methylene-blue as the indicator; another portion is then titrated in the presence of safranine or induline. The first titration gives the quantity of iron, the second that of the iron plus copper. All the titrations must be made in an atmosphere of carbon dioxide. The small amount of titanium trichloride required to reduce the indicators is estimated separately, and its quantity deducted from the total volume used for the titrations. W. P. S.

Causes of Error Affecting the Determinations of Atomic Weights. IV. Micro-analytical Method for the Study of Gases; Application to the Analysis of Traces of Air. PH. A. GUYE and F. E. E. GERMANN (*J. Chim. phys.*, 1916, **14**, 195—203).—A form of apparatus is described which the authors have employed with success in the analysis of small quantities of gases. It resembles in type the Orsat apparatus, but is designed for the examination of quantities of gas of the order of 0·1 c.c. The gas is submitted to the action of yellow phosphorus or iron wire heated to incandescence, and of solid potassium hydroxide, and the residue, after sparking between platinum electrodes, is subjected to the action of the discharge between aluminium electrodes, the discharge tube being protected from mercury vapour by the interposition of a small tube containing gold leaf. The manipulation and analysis of these small quantities of gases is rendered possible by operating on the gas at a pressure of about 1/100 of an atmosphere. H. M. D.

Destruction of the Organic Matter in Urine by Hydrogen Peroxide and the Estimation of Neutral Sulphur. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1915, **96**, 323—334).—The organic matter in the urine is destroyed when 500 c.c. of the urine, with the addition of 2 c.c. of hydrochloric acid and 200 c.c. of 3% hydrogen peroxide, are evaporated as completely as possible, first over the naked flame and then on the water-bath. On adding water to the gummy residue, traces of hydrogen peroxide are found to be still present, which may interfere with the subsequent estimation of certain substances, such as mercury.

By this process the neutral sulphur is oxidised partly to sulphate and partly to sulphite. It is therefore useless for the estimation of sulphur compounds in urine. H. W. B.

Rapid Method for the Estimation of Sulphates in Wine. J. PRITZKER (*Chem. Zeit.*, 1916, **40**, 499—501).—The quantity of sulphate present in a wine may be estimated approximately by measuring the volume of the barium sulphate precipitate formed when the wine is treated with barium chloride and submitted to centrifugal action. Four c.c. of the wine are placed in a tube the lower end of which is narrowed and graduated, 4 c.c. of water and 1 c.c. of 10% barium chloride solution containing hydrochloric acid are added, and the mixture is submitted to centrifugal action for three minutes. The narrow portion of the tube is so graduated that the volume of the precipitate indicates directly the sulphate as grams of potassium sulphate per litre of wine. More trustworthy results may be obtained by treating a definite volume of the wine with a quantity of standardised barium chloride solution insufficient to precipitate the whole of the sulphate, submitting the mixture to centrifugal action, and then adding a further quantity of 0·1 c.c. of the barium chloride solution. If a turbidity is produced, the mixture is again submitted to centrifugal action, and so on, until the whole of the sulphate has been precipitated; the total quantity of barium chloride solution added is a measure of the sulphate present. W. P. S.

Estimation of Phosphorus in Plant Materials. A. W. CHRISTIE (*J. Ind. Eng. Chem.*, 1916, **8**, 511).—Ignition with magnesium oxide is shown to be a trustworthy method of oxidising plant materials for the estimation of the total phosphorus content. W. P. S.

Estimation of the Citric Acid-soluble Phosphoric Acid in Thomas Slag by the Lorenz Method. O. LEMMERMANN (*Chem. Zentr.*, 1916, i, 721; from *Landw. Jahrbuch*, 1916, **49**, 159—160). —Remarks on the work of Dubbers and Celichewski (A., 1915, ii, 576). G. F. M.

New Form of Arsenic Apparatus. JOHN CHARLES HIBBERT (*J. Soc. Chem. Ind.*, 1916, **35**, 672—673).—A slightly modified form of apparatus for carrying out the quantitative Gutzeit test for arsenic consists of a generating bottle fitted with the usual tap funnel and with a 5 mm. upright tube, over the orifice of which a strip of mercuric chloride paper is held by means of a spring clip, and a celluloid or vulcanite plate perforated by a 5 mm. hole concentric with the bore of the tube and somewhat countersunk on the underside to ensure a gas-tight seal. The strip of paper has the advantage over the disk originally described in that in the event of a larger amount of arsenic than was anticipated being present, a series of stains can be obtained by shifting the strip along, and the total arsenic estimated by summation. The apparatus is conveniently set up in battery form, the requisite temperature being maintained either by electrical or steam heating. G. F. M.

Industrial Arsenical Poisoning. Detection of Arsenic in Hair, etc. G. MEILLÈRE (*J. Pharm. Chim.*, 1916, [vii], **14**, 5—8).—The hair (including that of the head and beard) of persons working in an arsenical atmosphere becomes impregnated, to a certain extent, with arsenic, and the detection of the latter in the hair affords a more certain means of safeguarding the health of the workers than does the detection of the element in the urine, fæces, etc. A portion of 2 grams of the hair should be treated with sulphuric and nitric acids to destroy the organic matter, the solution diluted with water, boiled to remove nitrous vapours, and then tested in a Marsh apparatus. W. P. S.

New Method for Testing the Adsorptive Power of Animal Charcoal and other Adsorption Agents. M. GUGGENHEIM (*Chem. Zentr.*, 1916, i, 595—596; from *Therap. Monatsheft.*, 1915, **29**, reprint, 4 pp.).—Guinea-pig intestines, isolated by the method of Magnus, can be used for testing the adsorptive power of animal charcoal, talc, etc. The presence of certain intestinal poisons, such as β-amino-4-ethylglyoxaline, can be conveniently demonstrated by the previously described method (this vol., i, 300). If the adsorption preparation is shaken with a solution of such a substance, it undergoes inactivation, and the quantity which is necessary to cause complete removal of the poison is inversely proportional to the adsorptive power of the preparation. G. F. M.

Method for Comparing the Decolorising Efficiency of Charcoals. LEONARD WICKENDEN and JOHN W. HASSLER (*J. Ind. Eng. Chem.*, 1916, **8**, 518—519).—Five grams of the charcoal are mixed with 100 c.c. of a 0·025% solution of aniline-red (Soudan III) in petroleum (kerosene) or a 0·1% solution of Oil Red RN in the same solvent; the mixture is then heated in a steam-bath for ten minutes with frequent stirring, filtered, and the colour of the filtrate compared with standards prepared by treating similar quantities of colour solution with varying amounts of a charcoal of average quality. A simple form of colorimeter for observing the colours is described. W. P. S.

A New Method for Estimating Carbon Monoxide in the Blood. K. L. GAD-ANDRESEN (*Biochem. Zeitsch.*, 1916, **74**, 357—370).—The total oxygen and carbon monoxide are driven from the laked blood by potassium ferricyanide. The mixed gases are then heated by a platinum wire, and the carbon monoxide is converted into the dioxide, which is absorbed by sodium hydroxide. The diminution of the volume is a measure of the amount of carbon monoxide. Barcroft's blood-analysis apparatus is employed for the estimation, but is so modified as to allow for the combustion of the carbon dioxide. For this purpose, electrically heated platinum wires are introduced through lead tubes into the blood-holders (the modified form of which is figured). The blood is laked with sodium hydroxide (0·05%), and the carbon dioxide formed by the com-

bustion is absorbed by 5% sodium hydroxide solution, of which a few drops are put on filter-paper attached to the stoppers.

S. B. S.

Water Analysis. III. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1916, **29**, i, 218—220. Compare this vol., ii, 194).—For the estimation of alkalinity, Wartha's method is recommended (titration of the boiling water with $N/10$-hydrochloric acid, using alizarin as the indicator), but iron salts, if present, must be removed previously; this method is also useful in detecting and estimating dissolved glass constituents in distilled water. If methyl-orange is used as the indicator, the water need not be boiled during the titration, but the end-point is not as sharp as with alizarin. A method is given for preparing standard calcium chloride solution from Iceland spar for use in standardising potassium oleate solutions employed in hardness estimations. A stable sodium sulphide solution for detecting the presence of heavy metals in waters may be prepared by dissolving 5 grams of crystallised sodium sulphide in 25 c.c. of water, adding 25 c.c. of glycerol, and filtering the mixture after twenty-four hours. The presence of methane in the gases separated from a water may be detected by treating the residue of gas, after the removal of the oxygen, with *iso*butyl alcohol previously saturated with air; if the residue of gas consists solely of nitrogen its volume does not decrease, whilst methane, if present, is absorbed. Details of manipulation in the estimation of dissolved oxygen are given, and a special form of tapped pipette is described.

W. P. S.

A Colorimetric Method used by the Romans for Characterising Soft Waters. MICHEL STEPHANIDES (*Compt. rend.*, 1916, **162**, 962).—A claim for priority over Trillat (compare this vol., ii, 269).

W. G.

A Method for the Estimation of very Small Amounts of Potassium. H. J. HAMBURGER (*Biochem. Zeitsch.*, 1916, **74**, 414—415).—The author calls attention to an error in the calibration of the capillary tubes used and described in his paper (this vol., ii, 50) on the estimation of potassium. With a correctly graduated instrument, each division = 0·0004 c.c. and corresponds with 0·000074059 gram of potassium.

S. B. S.

Estimation of Potassium in Presence of other Substances. ALEX. H. BENNETT (*Analyst*, 1916, **41**, 165—168).—Thin and Cumming (T., 1915, **107**, 361; A., 1915, ii, 281) have pointed out the possible sources of error and interference in the perchlorate method for the estimation of potassium, whilst Mitscherlich and Fischer (A., 1912, ii, 996) have shown that the composition of the precipitate obtained in the potassium sodium cobalt nitrite method is not constant. For the estimation of potassium in the presence of relatively large amounts of sodium and magnesium salts, the author recommends a combination of the two methods

mentioned; the precipitate obtained in the cobalt nitrite method is dissolved in hydrochloric acid, and the potassium in this solution then estimated by the perchlorate method. The cobalt reagent employed is prepared by dissolving 50 grams of cobalt nitrate and 300 grams of sodium nitrite in water, adding 25 c.c. of glacial acetic acid, diluting the solution to 1 litre, and filtering it after twenty-four hours. Thirty c.c. of the reagent are added to every 50 c.c. of the potassium salt solution; after two hours the precipitate is collected, washed with water containing a small quantity of the reagent, then dissolved in hot dilute hydrochloric acid, the solution filtered, and the filtrate and washings evaporated to dryness in a porcelain basin. The residue is dissolved in water, perchloric acid is added, the mixture evaporated, the residue, when cold, treated with 25 c.c. of 98% alcohol, and the insoluble portion collected on a filter, washed with alcohol containing 2% of perchloric acid, and saturated with potassium perchlorate, dried at 100°, and weighed. If the potassium salt solution under examination contains iron and aluminium phosphates, sodium citrate must be added to keep the phosphates in solution when the cobalt reagent is added. Ammonium salts must not be present. W. P. S.

Rapid Method for Estimating Calcium Oxide in Peat Soils. ROSS AIKEN GORTNER (*Soil Sci.*, 1916, **1**, 505—508).—The peat (5 grams) is ignited in a quartz dish, the ash digested with aqua regia, evaporated to dryness, extracted with dilute acid, filtered, and made up to 500 c.c. Of this solution, 100 c.c. are treated with ammonia to precipitate the iron and aluminium, boiled, and precipitated with 18 c.c. of a saturated solution of ammonium oxalate. After boiling for two minutes, the solution is left for at least three hours, filtered, and the precipitate washed. The precipitate is transferred to a beaker, the filter being washed with hot sulphuric acid, and after adding 10 c.c. of strong sulphuric acid the solution is heated nearly to boiling and titrated with permanganate (1 c.c. = 0·001 gram CaO).

The method is not suitable for mineral soils. N. H. J. M.

Separation of the usual Metals the Sulphides of which are Insoluble in Dilute Acids. J. CLARENS (*Bull. Soc. chim.*, 1916, [iv], **19**, 154—158).—The method is one of fractional precipitation with hydrogen sulphide from solutions of varying acidity. The solution is first neutralised, and then half its volume of concentrated hydrochloric acid is added and hydrogen sulphide is passed through the cold liquid. This precipitates copper, mercury, arsenic, and antimony. The filtrate is warmed and hydrogen sulphide again passed through it, any precipitate of arsenic sulphide or sulphur being filtered off. The filtrate is diluted with an equal volume of water, and a precipitate, on the further passage of hydrogen sulphide, indicates tin or bismuth or both. The filtrate from this precipitate is boiled for two or three minutes, neutralised with ammonia, acidified with a few drops of hydro-

chloric acid, and hydrogen sulphide passed through the cold solution. Any cadmium or lead present is precipitated at this stage. The three precipitates obtained in this way are subjected to further qualitative analysis by the usual methods. W. G.

Estimation of Lead as Lead Sulphite. H. PELLET (*Ann. Chim. anal.*, 1916, **21**, 114—116).—The lead solution is neutralised with sodium hydroxide, then rendered slightly acid with acetic acid and saturated with sulphur dioxide; the precipitated lead sulphite is collected on a weighed filter, washed, dried, and weighed. The weight of the precipitate is multiplied by 0·721 to obtain the equivalent quantity of lead. As lead sulphite is less soluble than lead carbonate, particularly in the presence of sugars, the method is especially useful for the estimation of lead in sugar solutions which have been clarified with lead acetate. Precipitation of lead as lead sulphite may also be employed for the separation of lead from other metals which are precipitated by hydrogen sulphide.
W. P. S.

Estimation of Small Quantities of Mercury in [Solutions of] Great Dilution. W. BÖTTGER and RICHARD HEINZE (*Zeitsch. Elektrochem.*, 1916, **22**, 69—71).—The present paper deals with the estimation of the total concentration of mercury in a saturated solution of calomel, the total concentration being required in order that the degree of ionisation and hydrolysis might be calculated from the conductivity values previously published (A., 1903, ii, 241). Two methods of estimating mercury in such cases are described; both methods depend on the formation of mercury diphenylcarbazide. In the first method, diphenylcarbazide is added to a measured volume of the solution, when a bluish-violet coloration is produced; on adding light petroleum and aluminium sulphate to the coloured solution, the mercury diphenylcarbazide is thrown out as a flocculent precipitate which collects on the boundary of the two liquids. The precipitate is collected on an asbestos filter, and, after washing, dissolved in nitric acid. The nitric acid solution is collected in a small, hard glass tube, sealed, and heated strongly to destroy the organic substances. The solution is then electrolysed, using a weighed gold wire as cathode. After suitable washing and drying, the wire is weighed on a microbalance. It is shown that, using 0·2 mg. of a mercury salt, this analysis can be effected with an accuracy of 5%; the addition of a little sodium carbonate to the diphenylcarbazide increases the accuracy, making it possible to obtain results which are accurate to 1%. In the second method resort is had to a spectrophotometric investigation of the blue-coloured solution of mercury diphenylcarbazide. The method consisted in determining the light absorption of a solution of mercury diphenylcarbazide by means of a Martens-Grünbaum spectrophotometer, and from a previously obtained concentration absorption curve reading off the concentration. An accuracy of 1% is obtained with solutions containing 0·01—1·0 mg. per litre. A saturated solution of calomel at 18°

contains 1·56 mg. of calomel per litre. The hydrogen-ion concentration is estimated by the indicator method to be $2·5 \times 10^{-6}$ gram-ion per litre, and the saturated solution at 25° had a specific conductivity of $2·33 \times 10^{-6}$ reciprocal ohms. J. F. S.

Colorimetric Method for the Detection of Manganese in Pigments, Varnishes, etc. J. F. SACHER (*Chem. Zentr.*, 1916, i, 438—439; from *Farbenzeit.*, 1915, **20**, 1309).—The reaction between manganese hydroxide and oxalic acid described previously by the author (A., 1915, ii, 495) may be used for the detection of manganese in pigments, paints, varnishes, etc. A small quantity of the substance is incinerated, the ash dissolved in water, and the solution filtered; the filtrate is rendered very slightly alkaline, heated gently, then cooled, and 3% oxalic acid is added drop by drop. A red coloration is obtained when just sufficient of the oxalic acid has been added to dissolve the manganese hydroxide. The test will detect as little as 0·05 mg. of manganese in 0·1 gram of substance. W. P. S.

Estimation of Tin in Tin Ashes. N. WELWART (*Chem. Zeit.*, 1916, **40**, 458—459).—An accurate estimation of tin in tin or white metal ashes, tin mud, tin ores, etc., is obtained by the following method. Three to ten grams of the sample are boiled with 30—100 c.c. of nitric acid (D 1·2), and when the evolution of nitrous fumes has ceased, three to four times the volume of boiling water are added, and the liquid is filtered. After washing with dilute nitric acid and water, filter and precipitate are ignited separately, weighed, and 0·3—0·35 gram of the crude stannic acid thus obtained assayed by fusing with a mixture of sodium hydroxide and sulphur (2:1) in a porcelain crucible, dissolving the fused mass in boiling hydrochloric acid (1:1), and when all the hydrogen sulphide has been expelled, reducing the solution in an atmosphere of carbon dioxide by means of pure antimony (2—2·5 grams), after the addition of 25 c.c. of concentrated hydrochloric acid. After cooling, the resulting solution of stannous chloride is titrated by means of $N/10$-iodine which has previously been empirically standardised against pure tin by dissolving it in concentrated sulphuric acid, diluting the solution with water, adding hydrochloric acid, and reducing as above with antimony and titrating with the iodine solution. The presence of other metals, such as lead, copper, or zinc, has no effect on the accuracy of the results, and the examples given show that with different workers they are trustworthy to within about 0·1%. G. F. M.

Volumetric Estimation of Tin by Potassium Iodate. GEORGE S. JAMIESON (*J. Ind. Eng. Chem.*, 1916, **8**, 500—502).—The method is based on the titration of precipitated tin or stannous chloride by potassium iodate solution. In the case of stannous chloride solution, the latter is placed in a stoppered bottle, concentrated

hydrochloric acid is added in quantity sufficient to make the actual HCl content at least 10%, a small quantity of chloroform is introduced, and standardised potassium iodate solution is added rapidly until the iodine colour has reached a maximum. The bottle is then stoppered, its contents shaken, and the titration continued until the violet coloration of the chloroform disappears. Stannic chloride solutions may be reduced by zinc and hydrochloric acid, and the metallic tin titrated as soon as the excess of zinc has dissolved. Sufficient potassium iodate must be added in the first instance to ensure the presence of free iodine or iodine monochloride in the solution, otherwise stannous chloride and hydrogen may be formed and cause an error. The stannic chloride may also be reduced by means of strips of nickel, the reduced solution being filtered through sand and cotton wool before titration. The method may be applied to the estimation of tin in alloys. Solder or type metal is dissolved in sulphuric acid, the solution boiled to expel sulphur dioxide, cooled, treated with hydrochloric acid, and the tin reduced and titrated as described. In the case of bronze, the tin is first separated as metastannic acid; this is dissolved in concentrated sulphuric acid, hydrochloric acid is added, and the estimation proceeded with as described. It must be remembered that cuprous, ferrous, and antimonious salts, as well as any precipitated metal, will react with potassium iodate.

W. P. S.

Estimation of Benzene and Toluene in Commercial Mixtures. A. EDWARDS (*J. Soc. Chem. Ind.*, 1916, **35**, 587—590).—The constituents of the naphtha are isolated in pairs, benzene–toluene and toluene–xylene, by fractional distillation, and from the boiling point of each pair its composition is obtained by reference to boiling point-composition curves, which were deduced from the respective vapour pressures and checked by determinations on admixtures of the pure constituents. The distillation is conducted under a 12-bulb Young column, the range 80·2° to 139° being divided into four parts, with refractionation of the two middle fractions up to 110·7°, the distillates going to the benzene–toluene pair and the residues to the toluene–xylene pair. Forerunnings must be separately collected up to 80·2° and refractionated. The boiling points of the fractions are then determined in a 50—120 c.c. wide-necked flask fitted with a reflux condenser and a ½-inch glass tube passing to within a short distance of the bottom of the flask, and having a hole blown in its side just below the cork to permit of the free circulation of the vapour. The thermometer passes down this tube, with its bulb about a quarter of an inch from the surface of the liquid, which is caused to boil up the bulb, and the temperature when constant is read off, corrected for barometric pressure and any thermometric error, and reference to the boiling point-composition curve constructed from the following table discloses the composition of the fraction:

Toluene. % by volume.	Boiling points. Benzene and toluene.	Toluene and xylene.
0	80·2°	139·0°
10	81·8	134·4
20	83·7	130·3
30	85·75	126·7
40	88·1	123·5
50	90·75	120·8
60	93·8	118·4
70	97·2	116·3
80	101·0	114·3
90	105·3	112·5
100	110·7	110·7

For tar distillation, an air-jacketed copper still, heated by indirect heat from a triple-ring burner, is recommended. For a rich tar containing up to 5% of water, a temperature of 230° in the jacket may usually be safely employed without danger of the contents of the still frothing up into the still-head, which should be at least 10 inches long. G. F. M.

Estimation of Benzene, Toluene, and Solvent Naphtha in Light Oils, etc. D. Wilson and I. Roberts (*J. Soc. Chem. Ind.*, 1916, **35**, 684—685; from *J. Gas Lighting*, 1916, **134**, 225—227). —An estimation of benzene and toluene in light oils is made by one fractional distillation of the washed and dried crude oil from a 2200 c.c. copper flask surmounted by a 40 in. × 1 in. Hempel column and a 21 in. × ½ in. Liebig condenser, which serves as a dephlegmator. The rate of distillation is first regulated to one drop per second, and the fraction collected to 79°. This may contain benzene, owing to the presence of water. The rate is then increased to 5 c.c. per minute, and the water leaving the dephlegmator kept below 80°. The fraction is collected to 81°, and consists of benzene. Again distillation is reduced to one drop per second, and an intermediate benzene–toluene fraction obtained up to 109°, the water in the dephlegmator being replaced as soon as it boils by a calcium chloride solution boiling at 105°. The fraction, 109—111·5°, distilled over at the higher rate is toluene, and the Hempel column is wrapped with asbestos paper while it is passing over. Finally, the calcium chloride solution is removed and a toluene–xylene intermediate fraction is collected up to 137°. Corrections for atmospheric pressure are made as follows: 81°, 0·043° per mm.; 109—111·5°, 0·047° per mm.; 137°, 0·052° per mm. The process is stated to give benzene and toluene boiling to within 1·5°; the intermediates are very small, and one fractional distillation will give the percentages to within a few tenths per cent., or the composition of the intermediates may be ascertained by distillation from a small flask. A mixture of 500 c.c. of benzene with 400 c.c. of toluene gave 498 c.c. of benzene and 398 c.c. of toluene. Paraffins are estimated by treating 10 c.c. with 25 c.c. of a mixture of two parts of sulphuric acid and one part of 20% fuming sulphuric acid. After cooling, the residual oil is driven into the

neck by pouring in sulphuric acid, and its volume read off on the graduations. G. F. M.

Detection of Free Mineral Acids in Wine. G. Bosco and R. Belasio (*Ann. Chim. Applicata*, 1916, **5**, 233—242).—This method is based on the fact that addition of a strong alkali to a strong acid results in diminution of the electrical conductivity, since the metallic ions are less mobile than those of hydrogen, whereas addition of a strong alkali to a weak acid leads to increase of the conductivity, the salt formed being more highly dissociated than the acid. Thus, addition of an alkali to a natural wine is accompanied by immediate increase of the conductivity, whilst when the wine contains free mineral acid this increase is preceded by a decrease. In practice it is found convenient to dilute one volume of the wine, after agitation to remove most of the carbon dioxide, to five volumes with distilled water. When the diluted liquid (25 c.c.) is introduced into the conductivity cell, care must be taken that gas bubbles do not adhere to the electrodes. The conductivity is measured in the ordinary way at constant temperature. Successive quantities of 0·1 c.c. of $N/10$-potassium hydroxide solution are then added to the cell, the liquid being mixed and the conductivity measured after each addition. Examples of the results obtained with both natural and plastered wines are given. T. H. P.

The Formaldehyde-Sulphuric Acid Reaction. Ernst Sieburg (*Biochem. Zeitsch.*, 1914, **74**, 371—375).—A résumé of colour reactions between aldehydes and phenols in the presence of sulphuric acid. S. B. S.

Amount of Sugar in Blood under Physiological and Pathological Conditions. III. O. Schumm (*Zeitsch. physiol. Chem.*, 1915, **96**, 204—235).—Various methods of estimating dextrose in blood are discussed, and the Lehmann-Maquenne method (compare Griesbach and Strassner, A., 1913, ii, 1082) is recommended. The residual reducing power of blood extracts which have been subjected to fermentation by yeast is due in some cases to unfermentable sugar arising from the yeast itself. H. W. B.

The Micro-method of Estimation of the Sugar of the Blood. Ivar Bang and E. Laurin (*Biochem. Zeitsch.*, 1916, **74**, 298—301).—In the employment of Bang's micro-method for the estimation of sugar, more accurate results are obtained when the proteins are coagulated (on filter-paper) with a cold solution of potassium chloride to which uranyl acetate has been added. This solution is prepared in the following way. To 1360 c.c. of saturated solution of pure potassium chloride are added 1·5 c.c. of 25% hydrochloric acid. Three grams of uranium acetate are dissolved in 200—300 c.c. of water, and these are added to the acid salt solution, and the mixture is then diluted to 2 litres. It has been

found that such a solution containing $1 \cdot 5^{\circ}/_{\circ\circ}$ of uranium salt suffices to produce complete coagulation of the proteins.

S. B. S.

Gravimetric Estimation of Reducing Sugars in Cane Products. GEORGE P. MEADE and JOSEPH B. HARRIS (*J. Ind. Eng. Chem.*, 1916, **8**, 504—509).—It is shown that the results obtained vary with the quantity of lead acetate solution used for clarifying the solutions. When the excess of lead is removed as oxalate, the weight of copper obtained is from 4 to 5% higher than when the lead is removed as sulphate or carbonate. A clear solution, suitable for copper reduction methods, may be obtained by treating the sugar solution with kieselguhr alone; the results are slightly lower than when lead and oxalate are employed. The cuprous oxide should be oxidised to cupric oxide, and weighed as such and not as cuprous oxide.

W. P. S.

Production and Excretion of Formic Acid. I. Estimation of Formic Acid in Pure Solutions and in Urine, together with a New Method for the Titration of Calomel. OTTO RIESSER (*Zeitsch. physiol. Chem.*, 1915, **96**, 355—366).—The solution (30 c.c.) containing the formic acid (10—20 mg.) is heated with a considerable excess of a solution containing 200 grams of mercuric chloride, 300 grams of sodium acetate, and 80 grams of sodium chloride per litre for six hours on the water-bath. The mixture is then cooled and, without filtering from the precipitated calomel, treated with 10 c.c. of 25% hydrochloric acid, then excess of concentrated aqueous potassium iodide (4 grams of potassium iodide for every 10 c.c. of the above mercuric chloride solution added to the formic acid solution), followed by an excess of $N/10$-iodine solution. The calomel is thereby quantitatively reconverted into mercuric chloride according to the equation $2HgCl + I_2 + 2HCl = 2HgCl_2 + 2HI$. The clear solution is now titrated with $N/10$-thiosulphate solution, employing starch as indicator in the usual way. The number of c.c. of $N/10$-iodine solution required to transform the calomel into mercuric chloride multiplied by 0·0023 represents the amount of formic acid in grams present in the volume of the solution taken for the analysis. In the absence of sodium chloride or a corresponding salt, the formic acid reduces a portion of the mercuric chloride to metallic mercury, whereby gross error in the estimation of the formic acid may be entailed; close adherence to the above conditions is therefore necessary.

The extraction of formic acid from urine is carried out by Dakin's method (A., 1913, i, 679), employing a rotating extraction apparatus. The subsequent estimation of the extracted formic acid is accomplished in the manner already described.

H. W. B.

Estimation of Small Quantities of Hydrocyanic Acid. MAXWELL O. JOHNSON (*J. Amer. Chem. Soc.*, 1916, **38**, 1230—1235).—In connexion with some work on cassava, the

author required a quick and accurate method of estimating small quantities of hydrocyanic acid. After studying various methods, a modification of Francis and Connell's thiocyanate method (A., 1913, i, 1284) was adopted.

The hydrogen cyanide is distilled into potassium hydroxide solution in the usual way, yellow ammonium sulphide is added, and the mixture evaporated to dryness. Potassium thiocyanate is extracted from the residue by repeated treatment with acetone. The acetone solution is evaporated to dryness, the residue dissolved in water, and shaken with ethyl acetate to remove organic colouring matter. The aqueous solution is then evaporated to dryness, and the residue dissolved in 50 c.c. of water and treated with 2 c.c. of 0·5% ferric chloride solution. The coloration produced is matched with that of a standard solution containing a known amount of potassium thiocyanate. E. G.

Detection of Salicylic Acid in Wine. X. ROCQUES (*Ann. Chim. anal.*, 1916, **21**, 117—118).—Twenty c.c. of the wine are placed in a 250 c.c. conical flask, 0·5 c.c. of dilute sulphuric acid (1:3) is added, and 15 c.c. of benzene are poured on the surface of the mixture; after about eighteen hours the benzene layer is transferred to a test-tube and agitated with 1 c.c. of dilute ferric chloride solution. If the wine contains as little as 2 mg. of salicylic acid per litre, the aqueous layer, after separation, exhibits a violet coloration. The presence of tannins, etc., in the wine does not interfere with the test. W. P. S.

Identification of Picric Acid in Urine. PECKER (*Ann. Chim. anal.*, 1916, **21**, 119—120; from *Soc. Biol.*, 1915).—Fifty c.c. of the urine are acidified with 5 c.c. of sulphuric acid (1:1), treated with a slight excess of 15% potassium permanganate solution, and the mixture is extracted with ether. The separated ethereal solution is dried with anhydrous sodium sulphate and evaporated. The residue, if coloured red, is evaporated with the addition of a few drops of nitric acid. Should the urine have contained picric acid or its decomposition products, the residue will have a yellow colour, and the picric acid may be identified by dyeing it on wool and applying the ammonium sulphide and potassium cyanide tests. Urine containing picric acid may be distinguished from icteric urine by the fact that it yields a yellow-coloured liquid after clarification with lead acetate; moreover, it does not contain albumin, biliary pigments, urobilin, or hæmoglobin. W. P. S.

New Salt of Uric Acid and its Application to the Analysis of Uric Acid and Phenol. J. LUCIEN MORRIS (*J. Biol. Chem.*, 1916, **25**, 205—210).—When a solution containing a small quantity of uric acid (1 mg. of uric acid in a litre of water) is acidified with acetic acid, treated with 10% zinc acetate solution, and then with saturated sodium carbonate solution until the reaction is alkaline to litmus, a flocculent precipitate of zinc

carbonate and zinc urate is produced, which can be readily collected, the filtrate being then quite free from uric acid. The uric acid in the precipitate is estimated by boiling with dilute acetic acid, adding a small amount of bismuth carbonate, and saturating with hydrogen sulphide. The precipitated sulphides are collected, and after removing the excess of hydrogen sulphide by boiling, the uric acid is measured colorimetrically by Benedict's modification of Folin's method (A., 1915, ii, 602).

The zinc urate has not been isolated, but under the conditions described above its precipitation is complete and practically instantaneous even from solutions of low concentration of uric acid. H. W. B.

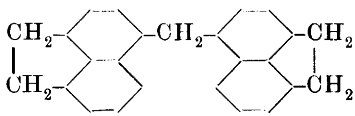
Colorimetric Method for the Estimation of Free Formaldehyde and Hexamethylenetetramine. R. J. COLLINS and P. J. HANZLIK (*J. Biol. Chem.*, 1916, **25**, 231—237).—The method consists in comparing the colour produced when the formaldehyde solution is treated with a solution of 0·1 gram of phloroglucinol in 10 c.c. of 10% sodium hydroxide with a series of standard colours prepared by mixing together prescribed volumes of 0·025% Congo-red and 0·01% methyl-orange solutions. A table showing the concentrations of formaldehyde which under the given conditions correspond with the respective standard colours is appended. The standard colours are not stable, and must be prepared freshly each day. The strength of the standard Congo-red solution is determined by comparison with a solution containing stated quantities of potassium dichromate and sulphuric acid. The method is found to be more accurate than the Romijn and other current methods.

Before applying the new method to the estimation of formaldehyde in urine, the phosphates must be removed by precipitation with a few drops of 50% sodium hydroxide solution, followed by filtration. When hexamethylenetetramine is present, the liquid must be distilled, and the free formaldehyde estimated in the filtrate. By estimating the formaldehyde before and after distillation, the respective quantities of free formaldehyde and hexamethylenetetramine are determined when both are present. H. W. B.

New Reaction of Aldehydes. R. DE FAZI (*Gazzetta*, 1916, **46**, i, 334—359).—The following reaction is the first capable of distinguishing between aromatic and aliphatic aldehydes. A few drops of a chloroform solution of acenaphthene (about 1%) are mixed with a solution of the aldehyde in chloroform and about 1 c.c. of concentrated sulphuric acid is slowly added. With an aromatic aldehyde a green ring, changing to reddish-violet, appears at the surface of separation above the sulphuric acid. If the liquid is shaken, it all becomes green, and subsequently reddish-violet, the latter coloration persisting for some days. Since the coloration is very intense, only a very small quantity of the aldehyde should be employed. The minimum amounts detectable

are: 0·0000078 gram benzaldehyde, 0·000019 gram vanillin, and 0·000006 gram furfuraldehyde. The reaction is given also by the aldoses, by sucrose, and by carbohydrates, such as cellulose, which yield furfuraldehyde or a similar aldehyde when treated with concentrated sulphuric acid in the cold.

Formaldehyde reacts with acenaphthene in presence of sulphuric acid, yielding a black, woody substance, which becomes green on prolonged washing with water and dirty yellow when left in the air. This reaction is probably similar to that occurring between formaldehyde and benzene, the compound formed having the structure



Acetaldehyde yields a similar condensation product.

The fusion diagrams of the systems formed by acenaphthene with vanillin, *p*-nitrobenzaldehyde, and piperonaldehyde respectively show that no compounds are formed. Each curve consists of two branches meeting at the respective eutectic points 67·5°, 66·8°, and 29·9°. Mixtures of acenaphthene and *p*-nitrobenzaldehyde are orange-yellow in the hot, but become colourless on cooling. T. H. P.

Estimation of Acetone in Systems of Methyl Alcohol, Water, and Potassium Fluoride, and Equilibria in Systems of Methyl Ethyl Ketone, Water, and Inorganic Salts. G. B. FRANKFORTER and LILLIAN COHEN (*J. Amer. Chem. Soc.*, 1916, **38**, 1136—1141).—In a paper on the equilibria in the system water, acetone, and inorganic salts (A., 1914, ii, 548) it was shown that acetone in aqueous solution could be estimated by means of potassium fluoride, and that it could also be estimated in methyl alcohol provided that the acetone was in excess of the alcohol. A study has now been made of the salting-out effect of potassium fluoride on solutions containing from 5 to 95% of methyl alcohol in water, and it has been found that it is not the amount of methyl alcohol, but rather the amount of acetone, which gives rise to discordant results. When not more than 18% of acetone is present it can be estimated by the method described (*loc. cit.*), but when a larger proportion is present the solution must be diluted, and the acetone can then be estimated without any interference being caused by the methyl alcohol.

Methyl ethyl ketone can be salted out from its aqueous solution by sodium chloride, potassium fluoride, or potassium carbonate, and the ketone can be estimated approximately, but not accurately, in this way. The following systems have been investigated and the binodal curve plotted for each: methyl ethyl ketone, water, and sodium chloride; methyl ethyl ketone, water, and potassium fluoride; methyl ethyl ketone, water, and potassium carbonate.

E. G.

Ninhydrin Reaction with Amino-acids and Ammonium Salts. VICTOR JOHN HARDING and FRANCIS H. S. WARNEFORD (*J. Biol. Chem.*, 1916, **25**, 319—335).—All ammonium salts under the right conditions are capable of giving a positive ninhydrin reaction. These conditions appear to be a faint alkalinity of solution, brought about either by the ammonium salt itself or by the presence of pyridine (A., 1915, ii, 382), and an adequate concentration of the ammonium salt. The colouring matter formed agrees in properties with the ammonium salt of diketohydrindylidenediketohydrindamine, prepared either synthetically or by the interaction of alanine and triketohydrindene hydrate. The reaction occurs with amino-acids more readily, and to a far greater extent than with ammonium salts.

The authors suggest that the first step in the interaction between amino-acids and triketohydrindene hydrate is the formation of ammonia and the corresponding glyoxal from the amino-acid (compare Dakin and Dudley, A., 1913, i, 925). The glyoxal then reduces the triketohydrindene hydrate to 1:3-diketohydrindole, which condenses with the ammonia liberated from the amino-acid to form 1:3-diketohydrindamine. This compound condenses with another molecule of triketohydrindene hydrate to give diketohydrindylidenediketohydrindamine, the ammonium salt of which possesses the observed blue colour (compare Ruhemann, T., 1911, **99**, 1486). When ammonia is present instead of the amino-acid, the triketohydrindene hydrate itself furnishes the necessary glyoxal (phenylglyoxal-*o*-carboxylic acid) under the influence of the weak alkali, and the reaction thus proceeds as above outlined. The ammonia must be dilute, otherwise the reaction proceeds in another direction (Ruhemann, T., 1910, **97**, 1438). It is found that the addition of reducing agents increases the ninhydrin reaction with ammonium salts. H. W. B.

Ninhydrin Reaction with Amines and Amides. VICTOR JOHN HARDING and REGINALD M. MACLEAN (*J. Biol. Chem.*, 1916, **25**, 337—350. Compare preceding abstract).—The ninhydrin reaction is given by organic bases of the types $CH_2R{\cdot}NH_2$ and $CHR_2{\cdot}NH_2$, where one radicle is negative in character. Other bases which readily yield ammonia or are readily oxidised may also give a positive reaction. Amides, guanidine, and derivatives of guanidine do not give a positive ninhydrin reaction.

It is evident from these results that the positive outfall of the ninhydrin test does not show definitely the presence of amino-acids. The most satisfactory method of applying the test appears to be to dilute the liquid to be tested until its concentration of nitrogen is 0·1 mg. per c.c., and then to heat 1 c.c. of the diluted liquid with 1 c.c. of 1% ninhydrin solution in a boiling-water bath for twenty minutes. The production of a blue colour, which shows a broad absorption band in the yellow region of the spectrum, indicates, in the majority of cases, the presence of an α-amino-acid. H. W. B.

New Reactions of Indican. ADOLF JOLLES (*Zeitsch. physiol. Chem.*, 1915, **95**, 29—33. Compare A., 1915, i, 1004).—The reactions involving the simultaneous oxidation of indoxyl and phenolic substances, leading to the formation of indigoid and indolignoid substances (*loc. cit.*), may be utilised as tests for indican in urine. For example, 10 c.c. of the urine are shaken with 1 c.c. of a 5% alcoholic solution of α-naphthol, 10 c.c. of fuming hydrochloric acid (D 1·19) containing 5 grams of ferric chloride per litre are added, and the mixture shaken and left for fifteen minutes. The dye is then extracted with 5 c.c. of chloroform, which is coloured violet to deep blue, according to the amount of indican present in the urine. H. W. B.

The Analysis of Proteins. I. The Estimation of Arginine by Decomposition with Alkali. ROBERT HENRY ADERS PLIMMER (*Biochem. J.*, 1916, **10**, 115—119).—The estimation of arginine in van Slyke's method can be effected by boiling the bases with 20% instead of 50% sodium hydroxide. The small deficiency of ammonia is counterbalanced by the ammonia due to a slight decomposition of histidine, which is greater in a copper than in a glass flask. When histidine is present, therefore, glass vessels should not be used for decomposition of arginine by alkalis.

S. B. S.

Estimation of the Total Protein and Non-protein Substances of Muscle. Improved Technique. N. W. JANNEY (*J. Biol. Chem.*, 1916, **25**, 177—183. Compare A., 1915, i, 1031).—The non-protein substances in muscle are removed by extraction with boiling alcohol and then with boiling water. The residue is collected on a tared filter-paper and again extracted in a Soxhlet apparatus, first with 95% alcohol for three hours and then with absolute alcohol for sixteen hours. The residual protein is dried at 105° and weighed. The total solids are estimated in the manner previously described, and the difference between the total solids and the total protein constitutes the non-protein substances.

H. W. B.

Recognition of Arginase by the Formaldehyde Method. S. EDELBACHER (*Zeitsch. physiol. Chem.*, 1915, **95**, 81—87).—See this vol., i, 524.

Valuation of Rhamnus Bark. LUDWIG KROEBER (*Chem. Zentr.*, 1916, i, 182; from *Apoth. Zeit.*, 1915, **30**, 605—606, 614—615).—The bark of *Rhamnus frangula*, on account of its greater anthraquinone content, more powerful action, greater cheapness, and better taste, is to be preferred to the officinal *R. purshiana*. The fluid extract of the latter drug is distinguishable from that of the former by characteristic reactions with tannic acid, ferric chloride, mercuric chloride, and ammonium molybdate and acetic acid. G. F. M.

General and Physical Chemistry.

The Relative Intensity of Gas Spectra in the Glow Discharge through Mixtures of Gases. J. FRANCK and G. HERTZ (*Ber. Deut. physikal. Ges.*, 1916, **18**, 213—220).—A theoretical discussion of the factors which determine the spectral emission of the glow discharge through tubes which contain two or more gases.

In accordance with the view that the spectrum of a gas will only make its appearance when this gas is ionised, it is to be expected that the ionisation potentials of the several gases in a mixture will determine the nature of the spectral emission. The spectrum of the gas with the smallest ionisation potential should be predominant, and this is found to agree with numerous observations on the emission from discharge tubes containing two or more gases of different ionisation potentials. The partial pressures of the gases are of comparatively little importance in connexion with the phenomenon.

It is possible to calculate the relative proportions of the two components of a gas mixture which undergo ionisation, and the calculation shows that the ratio of the numbers of the two kinds of ionised molecules, and consequently the ratio of the impurities of the spectra, depends mainly on the difference between the squares of the ionisation potentials, although the strength of the electrical field is also a factor which plays some part. Quantitative measurements suitable for testing the theoretical formula are not available, but it is apparent that this is qualitatively in accord with experiment. H. M. D.

The Distribution of Intensity in Broadened Spectrum Lines. J. W. NICHOLSON and T. R. MERTON (*Phil. Trans.*, 1916, [A], **216**, 459—488).—When gases at low pressures are excited by uncondensed electric discharges, the width of the spectrum lines emitted can be satisfactorily accounted for by the translatory motion of the radiating particles on the basis of the Doppler effect. When these conditions are departed from, the distribution of tho intensity in broadened spectrum lines is not at all in accordance with the requirements of the above method of explanation, and it is suggested that the cause of the broadening in these circumstances is connected with the Stark effect, according to which the radiations emitted by a luminous source in a powerful electrical field are resolved into components in a manner analogous to the Zeeman effect in a magnetic field.

In order to obtain further evidence in support of this view the distribution of intensity in broadened spectrum lines has been measured and compared with that calculated on the assumption that the broadening is electrical in origin. For this purpose a method has been devised, involving the use of a neutral-tinted glass wedge, cemented to a similar wedge of clear glass so as to form a

plane parallel plate, by means of which it has been found possible to measure accurately the intensity distribution in broadened lines.

Quantitative measurements have been made for the hydrogen line H_α and qualitative observations for other lines of hydrogen, helium, and lithium.

The most general characteristic of all the intensity distribution curves is that their curvature is away from the axis perpendicular to the wave-length scale. Even in the case of a simple curve, such as that obtained for H_α where the broadening is symmetrical, this is inconsistent with the view that a single component is involved. On the supposition that there are several electrically resolved components, symmetrically distributed about the centre, the only general law consistent with the curvatures of the intensity distribution curves is shown to be that expressed by a sum of linear exponential terms, one for each component. Intensity curves regulated by this law must show discontinuities in the slope of the curves, and those which have been found in the case of the line H_α are in quantitative accordance with those calculated from the available data for the electrical resolution.

The observations made on H_β and H_γ and the diffuse series of helium and lithium are also in qualitative agreement with the view that electrical resolution is the chief cause of the broadening of these spectral lines. H. M. D.

The Primary High Frequency Spectrum of Iodine and Tellurium. MANNE SIEGBAHN (*Ber. Deut. physikal. Ges.*, 1916, **18**, 39—40).—Previous measurements of the wave-lengths of lines in the high-frequency spectra of iodine and tellurium, made according to the secondary ray method, have led to opposite conclusions relative to the sequence of the elements in the scale of atomic numbers.

New determinations, made by the primary-ray method, have given $\lambda = 0{\cdot}437 \times 10^{-8}$ and $0{\cdot}388 \times 10^{-8}$ cm. for the wave-lengths of the α_1 and β_1 lines in the spectrum of iodine, the corresponding values for tellurium being $\lambda = 0{\cdot}456 \times 10^{-8}$ and $0{\cdot}404 \times 10^{-8}$ cm. These numbers satisfy Moseley's formula connecting the frequency with the atomic number, if the atomic numbers of tellurium and iodine are respectively 52 and 53. The sequence of the elements in the atomic number scale corresponds therefore with the chemical behaviour of the elements. H. M. D.

A New Series (l) in the High Frequency Spectra of the Elements. MANNE SIEGBAHN (*Ber. Deut. physikal. Ges.*, 1916, **18**, 150—153).—As a result of the examination of the spectral region $\lambda = 1{\cdot}0 \times 10^{-8}$ to $\lambda = 2{\cdot}30 \times 10^{-8}$ cm., the existence of a new series of lines has been established. This series is termed the l-series in order to connote its close relation to the well-known L-series. For each of the elements from tungsten to uranium, the spectrum contains a single line. The frequencies of these lines are connected with the atomic numbers by the Moseley formula, $\sqrt{\nu} = a(N - N_0)$.

H. M. D.

A Further Series (M Series) in the High Frequency Spectra of the Elements. MANNE SIEGBAHN (*Ber. Deut. physikal. Ges.*, 1916, **18**, 278—282. Compare preceding abstract).—As a result of the examination of the spectra of a number of elements of high atomic weight in the region $\lambda = 2$ to 10×10^{-8} cm., the author has found a new group of lines which has been distinguished as the *M* series. The wave-lengths of four to six lines belonging to this series have been measured in the spectra emitted by gold, thallium, lead, bismuth, thorium, and uranium. The frequencies of the strongest (α and β) lines are connected with the atomic numbers by Moseley's formula, but this does not seem to hold in the case of the weaker lines.

The *l*-line, referred to in the previous paper, belongs in all probability to the *L* series, forming a doublet with the η-line of the *L*-group. H. M. D.

The Rotation Spectrum of Water Vapour. H. RUBENS and G. HETTNER (*Ber. Deut. physikal. Ges.*, 1916, **18**, 154—167).—The absorption of water vapour in the region extending from $\lambda = 8\ \mu$ to $\lambda = 35\ \mu$ has been examined with the result that the number and position of the absorption bands are found to be in agreement with the requirements of the theory of quanta. The fact that the maxima of absorption are fairly broad and ill-defined is, however, considered to be contradictory to Bjerrum's theory that the absorption in this region is connected with the rotation of the molecules. On the other hand, it has been found that the absorption bands in the short-waved portion of the ultra-red region become narrower and more sharply defined when the gas pressure is reduced, an effect which is also observed with the series lines of the elements.

H. M. D.

The Absorptive Power of Aluminium Oxide. HILDEGARD MIETHING (*Ber. Deut. physikal. Ges.*, 1916, **18**, 201—212).—With a view to the employment of alumina for the measurement of high temperatures by the radiation method, the radiant properties of this substance at high temperatures have been investigated. The influence of foreign substances (ferric oxide and chromic oxide) on the behaviour of alumina was also examined.

A simple form of apparatus is described by means of which measurements of the absorption coefficient were made at temperatures between 1200° and 1600° for light rays of various wave-lengths. The results obtained show that the absorption-coefficient of pure aluminium oxide varies with the colour of the light, but is independent of the temperature. A similar result was obtained in presence of chromic oxide, but admixture of ferric oxide causes the absorption coefficient to change with the temperature.

Some results obtained with thoria and with porcelain are also communicated. H. M. D.

Rate of Loss of Activity of Illuminated Chlorine. MAX BODENSTEIN and HUGH STOTT TAYLOR (*Zeitsch. Elektrochem.*, 1916, **22**, 202—206).—Experiments have been made with the object of

ascertaining how long the activity produced by illuminating chlorine persists. For this purpose a stream of pure chlorine which had been illuminated was mixed with hydrogen and passed at a known rate through a blackened tube. The mixture of hydrogen and chlorine was then examined for hydrogen chloride. A series of similar experiments was made without first illuminating the chlorine. Comparison of the two sets of results indicate that there is no difference in the amount of hydrogen chloride contained in the gas mixture in either case. From these results it is calculated that the chlorine has completely lost its activity in 1/1600 second. It is suggested that statements in the literature which attribute a considerable period of existence to the active chlorine are based on experiments carried out with impure gases, and that the activity observed in these cases is due to some entirely different cause.

J. F. S.

Metal Fogs and Pyrosols. RICHARD LORENZ (*Kolloid. Zeitsch.*, 1916, **18**, 177—190).—A further account of work previously described (compare A., 1915, ii, 260, 261; this vol., ii, 207).

H. M. D.

Photochemical Phenomena. II. The Photo-oxidation of Alcohol with the Co-operation of Ketones. J. BÖESEKEN and W. D. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1640—1647).—In the formation of pinacones by the interaction of ketones and alcohols, it has been found that the alcohol is converted quantitatively into the corresponding aldehyde (or ketone), and not into the correlated pinacone. This is not only the case for aliphatic alcohols, but there is evidence that the mechanism of the reaction is the same when aromatic alcohols take part in the reaction.

Further observations on the photo-reaction in mixtures of alcohols with the phthalophenones have shown that the solution becomes yellow in colour, but that this colour disappears in the early stages when the mixture is shaken up in contact with the air, indicating that the yellow substance is oxidised by atmospheric oxygen. It is supposed that the ketone under the influence of violet rays reacts with the alcohol to form the yellow substance, and that the yellow substance is decomposed by the oxygen with the formation of the phthalophenone, aldehyde (or ketone), and water. Although the yellow substance is permanent in the dark and in the absence of oxygen, it is photo-sensitive, and by the further action of light is decomposed with the formation of the phthalophenopinacone and aldehyde (or ketone).

It is supposed that the mechanism of this photo-reaction bears some resemblance to the assimilation process.

Experiments in which a solution of benzophenone in dry ethyl ether was insolated showed that no reaction takes place, but with moist ether, pinacone and aldehyde are formed in accordance with the equation $4Ph\cdot CO\cdot Ph + Et_2O + H_2O = 2OH\cdot CPh_2\cdot CPh_2\cdot OH +$

$2CH_3 \cdot COH$. Apparently the photo-reaction induces the formation of alcohol in spite of the retarding influence of the water.

H. M. D.

Isotopes of Chemical Elements Collectively. A. VAN DER BROEK (*Physikal. Zeitsch.*, 1916, **17**, 260—262. Compare also "Is Proto-Oxygen the Principal Constituent of the Atoms?" A. van der Broek, *Nature*, 1916, **97**, 479).—From Moseley's experiments the mean difference between thorium and magnesium is 16 units of atomic weight for 6 of atomic number, $232 - 24 \div 16$ being the same as $90 - 12 \div 6$. From radio-actinium and from radiothorium the sequence of disintegration is α, α, α, α, β, β. But if the α-particle is the real constituent of atoms, $4\alpha + 2\beta$-particles is the oxygen nucleus (proto-oxygen), the additional 6 β-particles being electrons of valency. That the atomic weights are not twice the atomic number would be due to the formation of these proto-oxygen or θ-particles within the nucleus, and radioactivity would be due to the disintegration of these θ-particles into their constituents. The α-particles themselves may be $4H + 2\beta$, similar to the structure of the θ-particles $4\alpha + 2\beta$.

In the first paper a chart is given in which it is supposed that, from uranium, thorium, and actinium, the latter assumed to have the atomic weight 227, disintegrations, in the order 4α- and then 2β-particles, proceed until the initial two short periods are reached and then α-particles only. The atomic weight–atomic number curve of such a simple disintegration scheme, especially for actinium, resembles the curve for the actual elements in a striking way. The atomic weight of the actual element lies throughout among the atomic weights of the isotopes so derived from a uranium series $(4n + 2)$, a thorium series $(4n)$, and an actinium series $(4n + 3)$.

F. S.

The Volatilisation of Radium-C. STANISLAW LORIA (*Monatsh.*, 1916, **37**, 173—184. Compare this vol., ii, 169).—A careful comparison has been made of the volatility of radium-$B + C$ and thorium-$B + C$, and it has been found that within the errors of experiments these two pairs of isotopic elements exhibit identical behaviour. Radium-$B + C$ in equilibrium commence to volatilise from platinum in air at 770°, both at the same temperature. From 770° to 1100° always more of the B- than of the C-member volatilises. The proportions of radium-C volatilised at 800°, 900°, 1000°, and 1150° respectively are 20%, 30%, 70%, and 95%. The radium curve of volatilisation shows exactly the same form as that of thorium, being composed of two similar curves joining at 35%, 940°. The foregoing refers to the deposits obtained directly from the emanations. When the C-members are deposited on the platinum by electrolysis from solution, volatilisation does not commence until 900° is reached, but the curves for thorium and radium show a form similar to that previously obtained and are indistinguishable. This result was tested by experiments with a mixed radium-C and thorium-C preparation.

F. S.

The Hydrogen Ion Concentration of some Complex Polyhydroxyborate Solutions. J. Böeseken and A. H. Kerstjens (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1647—1653).—The influence of certain polyhydroxy-compounds on the hydrogen-ion concentration of boric acid solutions has been investigated by electrometric and conductivity measurements.

Mannitol and lactic acid give rise to an increased conductivity, and in support of the view that this is due to the formation of more readily ionised complex compounds it is found that the hydrogen potential measurements indicate an increase in the hydrogen-ion concentration.

With solutions containing catechol, pyrogallol, and hydroxyquinol it was observed that hydrogen is absorbed at the electrode and constant values for the potential difference are unattainable. In all cases, however, there is an increase in the conductivity when these substances are mixed with boric acid, and it is probable that stronger complex acids are formed. H. M. D.

The Electrical Conductivity of Liquid Metals and Alloys in its Relation to the Electron Concentration and the Viscosity. Franz Skaupy (*Ber. Deut. physikal. Ges.*, 1916, **18**, 252—260).—On the assumption that the difference in the electrical conductivity of a dilute amalgam and free mercury is due to the ionisation of the dissolved metal, and that the conductivity is inversely proportional to the viscosity, the conductivity L of an amalgam in terms of that of mercury may be represented by the formula

$$L=\eta/\eta_1\cdot(1+a[M^{\cdot}]),$$

in which $[M^{\cdot}]$ is the concentration of the metal ions, η and η_1 are the viscosity-coefficients of pure mercury and the amalgam, and a is a constant. The values of a for different metals show that this increases with the electro-positive character of the metal. For the alkali metals the increase is evident from the following numbers: lithium, 17; sodium, 18; potassium, 28; rubidium, 32; cæsium, 53. On account of the small differences between these coefficients it is supposed that the metals dissolved in the mercury are ionised to a considerable extent.

It is shown that the degree of ionisation of pure liquid mercury may be calculated from its conductivity in combination with the conductivity of an amalgam, for which the value of a is known. The value thus obtained is 0·02, which appears to be of the right order of magnitude, in that the application of Stokes's formula to calculate the radius of the electron yields an approximately correct result when the mercury is supposed to be ionised to the extent of 2%.

By application of the thermodynamic formula for the influence of temperature on the ionisation equilibrium, it may be shown that the atomic heat of ionisation is approximately 2000 cal.

For other liquid metals very few data are available, but zinc, lead, and bismuth appear to be appreciably ionised if Stokes's formula may be applied to the movement of the electrons.

The view that fused metallic solutions are analogous to solutions

of electrolytes is, of course, met with the objection that transport experiments have in most cases afforded no evidence of changes in concentration, but it is shown that this is not necessarily antagonistic to the theory of liquid metals which is advocated. H. M. D.

Measurements of the Conductivity of Organic Acids. RUD. WEGSCHEIDER (*Monatsh.*, 1916, **37**, 219—250).—The electrical conductivity of aqueous solutions of a number of organic acids has been measured at 25°. In the following summary the values of the ionisation constant (K) and of the molecular conductivity λ_{∞} at infinite dilution are recorded.

Phthaldehydic acid, $K=0{\cdot}00312$, $\lambda_{\infty}=378{\cdot}7$; bromo-opianic acid, $K=0{\cdot}00434$, $\lambda_{\infty}=375$; 2-ethyl 1-hydrogen 4-nitrophthalate, $K=0{\cdot}52$, $\lambda_{\infty}=374{\cdot}8$; 1-ethyl 2 hydrogen 4-nitrophthalate, $K=0{\cdot}305$, $\lambda_{\infty}=374{\cdot}8$; 1-methyl 2-hydrogen 4-hydroxyphthalate, $K=0{\cdot}0154$, $\lambda_{\infty}=376$; 1-ethyl 2-hydrogen 4-hydroxyphthalate, $K=0{\cdot}073$, $\lambda_{\infty}=375$; 2-ethyl 1-hydrogen 4-hydroxyphthalate, $K=0{\cdot}022$, $\lambda_{\infty}=375$.

Methyl hydrogen *iso*phthalate, $K=0{\cdot}0128$, $\lambda_{\infty}=376{\cdot}5$; 4-nitro*iso*phthalic acid, $K=1{\cdot}03$, $\lambda_{\infty}=377$; 3-methyl 1-hydrogen 4-nitro*iso*phthalate, $K=0{\cdot}084$, $\lambda_{\infty}=375{\cdot}7$; 1-methyl 3-hydrogen 4-nitro*iso*phthalate, $K=1{\cdot}09$, $\lambda_{\infty}=375{\cdot}7$; 1-methyl 3-hydrogen 4-amino*iso*phthalate, $K=0{\cdot}0044$, $\lambda_{\infty}=375{\cdot}7$; 1-ethyl 3-hydrogen 4-amino*iso*phthalate, $K=0{\cdot}0040$, $\lambda_{\infty}=374{\cdot}8$; 3-methyl 1-hydrogen 4-amino*iso*phthalate, $K=0{\cdot}00267$, $\lambda_{\infty}=375{\cdot}7$; 4-dimethylamino-*iso*phthalic acid, $K=0{\cdot}0265$, $\lambda_{\infty}=374{\cdot}8$; 1-methyl 3-hydrogen 4-dimethylamino*iso*phthalate, $K=0{\cdot}000056$, $\lambda_{\infty}=374{\cdot}2$; 3-methyl 1-hydrogen 4-dimethylamino*iso*phthalate, $K=0{\cdot}003$, $\lambda_{\infty}=374{\cdot}2$.

1-Methyl 3-hydrogen 4-aceyltamino*iso*phthalate, $K=0{\cdot}069$, $\lambda_{\infty}=374{\cdot}4$; 4-acetylmethylamino*iso*phthalic acid, $K=0{\cdot}072$, $\lambda_{\infty}=374{\cdot}4$.

1-Methyl 4-hydrogen 2-methylterephthalate, $K=0{\cdot}0156$, $\lambda_{\infty}=375{\cdot}3$; 4-methyl 1-hydrogen 2-methylterephthalate, $K=0{\cdot}055$, $\lambda_{\infty}=375{\cdot}3$; 1-methyl 4-hydrogen 2-aminoterephthalate, $K=0{\cdot}015$, $\lambda_{\infty}=375{\cdot}7$; methylaminoterephthalic acid, $K=0{\cdot}028$, $\lambda_{\infty}=375{\cdot}7$; 4-methyl 1-hydrogen 2-methylaminoterephthalate, $K=0{\cdot}0036$, $\lambda_{\infty}=374{\cdot}8$; 2-dimethylaminoterephthalic acid, $K=0{\cdot}045$, $\lambda_{\infty}=374{\cdot}8$; 1-methyl 4-hydrogen 2-dimethylaminoterephthalic acid, $K=0{\cdot}0004$ (?), $\lambda_{\infty}=374{\cdot}2$; 4-methyl 1-hydrogen 2-dimethylaminoterephthalate, $K=0{\cdot}00003$, $\lambda_{\infty}=374{\cdot}2$.

Anhydroacetylaminoterephthalic [acetylanthranilcarboxylic] acid, $K=0{\cdot}079$, $\lambda_{\infty}=375$; 1-methyl 4-hydrogen 2-acetylaminoterephthalate, $K=0{\cdot}0261$, $\lambda_{\infty}=374{\cdot}4$; 4-methyl 1-hydrogen 2-acetylaminoterephthalate, $K=0{\cdot}072$, $\lambda_{\infty}=374{\cdot}4$; acetylmethylaminoterephthalic acid, $K=0{\cdot}14$, $\lambda_{\infty}=374{\cdot}4$.

Trimellitic acid, $K=0{\cdot}32$, $\lambda_{\infty}=376{\cdot}5$; 1-methyl 2 : 4-dihydrogen trimellitate, $K=0{\cdot}18$, $\lambda_{\infty}=375{\cdot}3$; 2-methyl 1 : 4-dihydrogen trimellitate, $K=0{\cdot}26$; 4-methyl 1 : 2-dihydrogen trimellitate, $K=0{\cdot}289$; 1 : 2-dimethyl 4-hydrogen trimellitate, $K=0{\cdot}034$, $\lambda_{\infty}=374{\cdot}6$; 1-mellitamic acid, $K=0{\cdot}044$, $\lambda_{\infty}=376$; 2-mellitamic acid, $K=0{\cdot}076$, $\lambda_{\infty}=376$; 5 : 6-dinitro-2 : 3-dimethoxybenzoic acid, $K=4{\cdot}6$, $\lambda_{\infty}=374{\cdot}6$; 6-nitro-*m*-toluic acid, $K=0{\cdot}031$, $\lambda_{\infty}=377$; *p*-sulphobenzoic acid, $K=50$ (?), $\lambda_{\infty}=380$; a-methyl *p*-sulphobenzoate, $K=0{\cdot}072$, $\lambda_{\infty}=378$; β-chrysenic

acid, $K = 0.093$, $\lambda_{\infty} = 373.9$; chrysodiphenic acid, $K = 0.16$, λ_{∞} 373·5; β-ethyl hydrogen aspartate, K decreases from 0·00069 at $v = 100$ to 0·000476 at $v = 1200$ in agreement with its amphoteric character.

The observed values of K are compared with those calculated from the constants of the unsubstituted acids by means of the factors which express the influence of the substituent groups, and although in some cases the agreement is satisfactory, there are others in which the divergence is very considerable.

Attention is directed to the low values of the ionisation constants of certain hydroxyphthalic acids, and it is suggested that this is due to tautomeric change resulting in the formation of hydroxy-lactones. This is supposed to be the cause of the anomalous behaviour of the methyl hydrogen esters of 4-hydroxyphthalic acid as compared with the corresponding ethyl hydrogen esters.

H. M. D.

The Stepwise Dissociation of Dibasic Acids. III. RUD. WEGSCHEIDER (*Monatsh.*, 1916, **37**, 251—259).—In previous papers (A., 1902, ii, 643; 1906, ii, 73) formulæ have been derived from which it is possible to calculate the constants characteristic of the first and second stages of the ionisation from the data for the conductivity of the acid at different dilutions. A more accurate expression for the concentration of the bivalent anion is now put forward, and it is shown that the ionisation constants may be more conveniently calculated by making use of the method of least squares. The dibasic acids which are strongly ionised, a method of calculation is described in which the constant for the second stage is calculated from the data for higher dilutions, and this constant is then made use of in the derivation of the constant for the first stage of the ionisation process. H. M. D.

The Electrolytic Dissociation of Tribasic Acids and the Derived Ester Acids. RUD. WEGSCHEIDER (*Monatsh.*, 1916, **37**, 261—276).—The law of mass action has been applied to the three successive stages involved in the complete ionisation of tribasic acids, and formulæ are given showing the relation between the total ionisation constants and the constants which are characteristic of the component processes which result in the formation of isomeric uni- and bi-valent anions. It is shown that the relative quantities of the isomeric ions may be calculated. The formulæ are applied to obtain the relation between the ionisation constants of the free acid and the derived ester acids. On the assumption of the usual factors for the influence of substituents on the ionisation constant, it is shown that the sum of the constants for the first stage of the ionisation of the three isomeric mono-ester acids is approximately equal to twice the constant for the first stage of the ionisation of the free acids, and further that the sum of the constants for the ionisation of the three isomeric diester acids is approximately equal to the constant for the first stage of the ionisation of the free acid.

The data obtained for the ionisation of trimellitic acid and its derived methyl ester acids are considered from the point of view of the theoretical formulæ. H. M. D.

The Separation of Gas Mixtures under the Influence of a Direct Current. Franz Skaupy (*Ber. Deut. physikal. Ges.*, 1916, **18**, 230—232).—When a fairly strong current is passed through a discharge tube containing neon mixed with about 10% of argon the anode end of the tube shows the neon spectrum and the cathode end the argon spectrum. Mixtures of helium and argon behave similarly, and further experiments have shown that the separation of gases under the influence of a direct current is a general phenomenon. If the mixture is supplied at the middle of the discharge tube and the gases in the neighbourhood of the electrodes are removed, it is possible to effect a separation of the inert gases.

When mercury or other vapours are mixed with the inert gases and subjected to the discharge, the active gases are always found to move to the cathode. The observed behaviour is apparently determined by the magnitude of the ionisation potential. A low value of the ionisation potential results in the production of large quantities of positive ions, whilst such ions may not be found at all when the ionisation potential has a larger value. The positive ions move to the cathode, and under the influence of the difference of gas pressure the unchanged molecules are constrained to move in the opposite direction.

In consequence of the above described effects, it follows that gases or vapours (for example, salt vapour) introduced into a discharge tube containing inert gases through which a direct current is passing will only produce a satisfactory emissive effect if they are introduced at the anode.

It is suggested that the electrical method of separation may find application in the investigation of neon, which has been supposed to consist of isotopes of atomic weight 20 and 22 respectively.

H. M. D.

The Validity of Faraday's Law for Flame Electrolytes. Bruno Thieme (*Ber. Deut. physikal. Ges.*, 1916, **18**, 187—194).—Experiments are described in which the quantity of carbon deposited by the passage of a current through a hydrocarbon flame has been measured. The best results are obtained when the air supply is only just sufficient to prevent the separation of soot. As the mean of several experiments with different current strengths, it is found that the quantity of electrolytically deposited carbon is in fair agreement with the requirements of Faraday's law if the carbon atoms are supposed to carry a single unit of charge.

H. M. D.

Faraday's Law and the Electrolytic Separation of Copper from Flames. Bruno Thieme (*Ber. Deut physikal. Ges.*, 1916, **18**, 221—229).—From experiments made with a flame sprayed with a solution of copper sulphate it is found that copper is deposited by an electric current passed through the flame in quantities consonant with Faraday's law. H. M. D.

Experimental Determination of Chemical Constants. W. Nernst (*Zeitsch. Elektrochem.*, 1916, **22**, 185—194).—A theoreti-

cal paper, in which the chemical constant of a gas is discussed. It is shown that in order to determine this quantity it is necessary that the following three quantities must be known: (i) The heat change of a chemical or physico-chemical reaction at a given temperature; (ii) the equilibrium of the given reaction at the same temperature; and (iii) the specific heat of all the reacting substances of this reaction from the reaction temperature down to absolute zero. It is also shown that all the molecular considerations put forward up to the present are agreed in the one point that the chemical constant of monatomic gases is expressed by $C = C_0 + 1{\cdot}5 \log M$, in which M is the molecular weight. The same expression holds for the other gases, but in applying it in these cases the loss of rotational energy at low temperatures must be known. At present this quantity is only known with sufficient accuracy in the case of hydrogen. The values of C and C_0 have been calculated from known data for the cases of mercury, argon, hydrogen, and iodine. The following values have been obtained: mercury, C, $1{\cdot}83 \pm 0{\cdot}03$, C_0, $-1{\cdot}62 \pm 0{\cdot}03$; argon, C, $0{\cdot}75 \pm 0{\cdot}06$, C_0, $-1{\cdot}65 \pm 0{\cdot}06$; hydrogen, C, $-1{\cdot}30 \pm 0{\cdot}15$, C_0, $-1{\cdot}76 \pm 0{\cdot}15$; and iodine, C, $1{\cdot}4$—$2{\cdot}8$, C_0, $-1{\cdot}8$—$-0{\cdot}4$. From these values it follows that $C = -1{\cdot}62 \pm 0{\cdot}03 + 1{\cdot}5 \log M$ when the atmosphere is taken as the unit of pressure; if, however, absolute units are taken, $C_0 = 4{\cdot}39 \pm 0{\cdot}03$. Of the many expressions for C, only those of Sackur-Tetrode, $C = \log (2\pi m)^{3/2} . k^{5/2}/h^3 = -1{\cdot}608 + 1{\cdot}5 \log M$, and that of the author, $C = \log (4\pi m)^{3/2} . k^{5/2}/eh^3 = -1{\cdot}590 + 1{\cdot}5 \log M$, are in keeping with the above relationships. Both these theories are based on the Nernst heat theory, and it is held that the calculations made in the present paper afford new proof of the truth of this theory.

J. F. S.

The Thermal Behaviour of Certain Compressed and Condensed Gases at Low Temperatures. A. EUCKEN (*Ber. Deut. physikal. Ges.*, 1916, **18**, 4—17).—Calorimetric experiments are described, in which the author has measured the specific heats of argon, nitrogen, oxygen, and carbon monoxide in the solid and liquid states and the specific heats of carbon dioxide in the solid state, of hydrogen in the liquid and gaseous states, and of helium in the gaseous state, the gases being subjected to high pressures in small steel bombs. The heats of liquefaction and of vaporisation and in some cases the heats of transformation from one solid form to another were also measured.

The molecular heats of liquefaction recorded are: argon, 267·9; nitrogen, 168·7; oxygen, 105·5; carbon monoxide, 224·1. Nitrogen exists in two solid forms with a transition temperature at 35·5° (abs.) and the molecular heat of transformation is 53·8. Oxygen occurs in three solid forms with transition temperatures at 23·5° and 42·5° (abs.). The heats of transformation are 17·5 and 167·4 respectively. There are also two forms of carbon monoxide with a transition temperature at 60·4° (abs.) and the heat of transformation is 144·1.

The recorded molecular heats of vaporisation are: hydrogen, 229;

nitrogen, 1363; oxygen, 1599; argon, 1501; and carbon monoxide, 1414. H. M. D.

Thermoelectric Measurement of the Critical Points of Iron. GEORGE K. BURGESS and H. SCOTT (*Compt. rend.*, 1916, **163**, 30—32).—By an arrangement already described (compare Burgess and Crowe, A., 1913, ii, 711), using a very pure specimen of iron (99·968%), the authors find that, contrary to the results of Benedicks (compare this vol., ii, 172), thermoelectric measurements indicate both the critical points A_2 and A_3. W. G.

Energy Changes in Binary Systems. VII. The Heats of Mixing of Binary Mixtures. ROBERT KREMANN (*Monatsh.*, 1916, **37**, 11—24).—A comparison has been made of the heat changes which have been found to occur in the mixing of certain pairs of substances with the values calculated from the equation

$$W = n_1 n_2 / b \,.\, (b_2\sqrt{a_1} - b_1\sqrt{a_2})^2 / b_1 b_2,$$

in which n_1 and n_2 represent the number of mols. of the two substances concerned, a_1, b_1 and a_2, b_2 the van der Waals' constants for the two components, and b the value of the co-volume for the mixture. The approximate agreement between the observed and calculated heat changes for the following pairs of substances: *o*- and *m*-xylene, *o*- and *p*-xylene, *m*- and *p*-xylene, benzene and ethylene dichloride, chlorobenzene and bromobenzene, dimethylaniline and *m*-xylene, methyl acetate and ethyl acetate, propyl acetate and amyl formate, nitrobenzene and ethylaniline, is supposed to indicate that these may be regarded as normal mixtures, and on this account may be used as standard combinations in the investigation of property composition curves. H. M. D.

A Simple Relation Involving the Heat of Vaporisation of Substances for which the Reduced Gas Constant $R_c = 3\frac{3}{8}$. LÉON SCHAMES (*Ber. Deut. physikal. Ges.*, 1916, **18**, 35—38).—Substances for which the reduced gas constant, $R_c = RT_c/p_c v_c = 27/8$, are shown to exhibit a relation between the density and the latent heat which is expressed by $d_1/d_2 = L_1/L_2$, in which d_1 and d_2 are the densities of the liquid and solid respectively and L_1 and L_2 the latent heats of vaporisation and sublimation. H. M. D.

The Viscosity of Liquefied Gases. IV. Apparatus and Method. V. Preliminary Measurements on Liquid Mixtures of Oxygen and Nitrogen. J. E. VERSCHAFFELT and CH. NICAISE (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1659—1675).—The method employed in these viscosity measurements depends on the determination of the logarithmic decrement of the oscillations of a carefully turned metal sphere suspended in the liquid. For liquid air at 79·6° (absolute) the coefficient of viscosity thus obtained is 0·001678. Values are also recorded for other gas mixtures as follows: O, 61%; N, 36%; Ar, 3%; $\eta = 0·001865$; O, 9·5%; N, 89%; Ar, 1·5%; $\eta = 0·001599$; O, 96%, N, 1%; Ar, 3%; $\eta = 0·001895$. H. M. D.

Energy Changes in Binary Systems. V. Constitution of the Ternary System *m*-Cresol–Aniline–Benzene According to Viscosity Measurements. R. KREMANN and VOJISLAV BORJANOVICS (*Monatsh.*, 1916, **37**, 59—84).—According to freezing-point measurements, *m*-cresol and aniline form an equimolecular compound, and this compound would also seem to be indicated by the viscosity-composition curve which shows a maximum. The position of this maximum does not correspond with the equimolecular mixture of the components, and it shifts with the temperature, but this discrepancy is attributed to the simultaneous dissociation of complex molecules of *m*-cresol.

In order to obtain further information on the question of the interpretation of viscosity-composition curves, the changes in the viscosity of *m*-cresol–aniline mixtures produced by the addition of an inert substance have been submitted to detailed investigation.

That benzene does not form compounds with *m*-cresol or aniline is shown by the freezing-point diagrams which in each case consist of two curves meeting in the eutectic point. The eutectic for *m*-cresol and benzene lies at $-22°$ and 61 mols. % of *m*-cresol. For the system aniline–benzene the eutectic is at $-33·5$, and the mixture contains 67 mols. % of aniline.

In the examination of the ternary system, binary mixtures containing fixed quantities of *m*-cresol and aniline were mixed with varying quantities of benzene. The curves which are obtained by suitably plotting the experimental data lead to the conclusion that the change in the character of the viscosity curves which is brought about by the addition of gradually increasing quantities of benzene at constant temperature is similar to the change which occurs in the curve for the binary mixture *m*-cresol and aniline when the temperature is raised.

This is in agreement with the view that the form of the binary viscosity curve is determined by the constitution of the mixtures, and is opposed to the view that the temperature effect is determined by the difference in the temperature-coefficients for the components of the mixture. H. M. D.

Energy Changes in Binary Systems. VI. Constitution of the Ternary System *m*-Cresol–Dimethylaniline–Benzene. R. KREMANN and N. SCHNIDERSCHITSCH (*Monatsh.*, 1916, **37**, 1—10). —According to experiments with mixtures of *m*-cresol and aniline, rise of temperature and isothermal dilution with benzene produce a similar alteration in the character of the viscosity curves (compare preceding abstract). In a further comparison of these effects, measurements have been made of the viscosities of mixtures of *m*-cresol and dimethylaniline with the addition of varying quantities of benzene.

At lower temperatures the viscosity curve for mixtures of *m*-cresol and dimethylaniline is of the sagged type. As the temperature rises the curve becomes inflected near the cresol end, and at still higher temperatures (about 100°) the cresol end of the curve lies above the straight line corresponding with the mixture rule.

It is supposed that the resulting sinuous character of the curve is due to the predominance of the influence of compound formation over the influence of molecular dissociation of the cresol complexes, to which is due the sagged nature of the curve at lower temperatures.

The results obtained for the viscosity of ternary mixtures with benzene as the third component indicate that isothermal dilution of a given mixture of *m*-cresol and dimethylaniline with benzene has a similar influence to that produced in the binary mixture by a rise of temperature. As the proportion of benzene increases, the sagging diminishes, and ultimately positive deviations from the requirements of the mixture rule become apparent at the cresol end of the series of binary mixtures. H. M. D.

Theoretical Considerations with Respect to the Viscosity of Colloids. H. VON SMOLUCHOWSKI (*Kolloid Zeitsch.*, 1916, **18**, 190—195).—According to Einstein the viscosity of a suspensoid or emulsion is represented by the formula $\eta = \eta_0(1 + 5/2 . \phi)$, where η_0 is the viscosity of the dispersive medium and ϕ is the fraction of the total volume which is occupied by the disperse phase. The application of this formula is strictly limited to systems in which the particles of the disperse phase are spherical. If the form of the particles is other than spherical, the value of the ratio η/η_0 for a given value of ϕ is greater than that given by the above formula.

It is also probable that the formula no longer holds if the size of the particles falls below a certain limiting value, for the formula is derived on the assumption that the radius of the particles is very large in comparison with the radius of the action of molecular forces. The relatively greater viscosity of highly disperse colloids in comparison with the viscosity of equally concentrated solutions of medium degree of dispersity affords evidence for the hypothesis that the formula is no longer applicable to the former. To bring the formula into line with experiment, Hatschek has assumed that each particle is surrounded by an envelope of the dispersive medium (adsorption film) of constant thickness, but there is no evidence in support of this view.

A further restriction imposed by the viscosity formula is that the value of ϕ must not be too large. If the concentration of the colloid is such that the radius of the particles is no longer small in comparison with the mean distance between the particles, it is probable that the influence of ϕ on the viscosity must be represented by a formula which involves higher forms of ϕ from the first. The data obtained by Odin for concentrated solutions of colloidal sulphur may, in fact, be represented with fair approximation by the formula $\eta = \eta_0/(1 - \phi - 3/2\phi^{5/3})^{5/2}$. The formula proposed by Hatschek (A., 1911, ii, 98) for concentrated colloidal solutions, which may be written in the form $\eta = \eta_0(1 - \sqrt[3]{\phi})$, cannot be regarded as more than a purely empirical formula.

On various occasions it has been suggested that the increase in viscosity on coagulation of a colloid is directly opposed to Einstein's formula. This increase may, however, be partly due to the forma-

tion of non-spherical aggregates which for the same value of ϕ would result in an increased viscosity. Even if the aggregates are approximately spherical, the fact that the total volume of such an aggregate is at least $3\sqrt{2}/\pi = 1{\cdot}35$ times greater than the sum of the volumes of the component particles must result in an increase in the viscosity.

A greater difficulty is presented by cases where the addition of small quantities of an electrolyte results in the diminution of the viscosity of the colloidal solution. This may be due to a reduction in the volume of the disperse phase (diminution of ϕ) or it may be connected with electrical endosmotic phenomena. H. M. D.

Adsorption of Gases (Vapours) by a Solid Non-volatile Adsorbent. M. POLÁNYI (*Ber. Deut. physikal. Ges.*, 1916, **18**, 55—80).—A theoretical paper in which the author discusses the connexion between the adsorption of gases, pressure, and temperature on the assumption that the adsorption is due to the surface concentration of the gas under the influence of the attractive forces which operate between the molecules of the gas and the adsorbent. It is shown that if the adsorption isotherm has been determined for any temperature, the conditions of equilibrium can be calculated for any other temperature and pressure provided that the constants of the equation of state are known. The variation of the concentration of the gas in the adsorption layer may also be determined. H. M. D.

Adsorption Phenomena in the Precipitation of Calcium Carbonate from a Carbonate Water. ALBERT REICHARD (*Kolloid. Zeitsch.*, 1916, **18**, 195—201).—Experiments are described which show that the precipitation of calcium carbonate from Munich supply water in consequence of the removal of carbon dioxide is appreciably influenced by the presence of foreign substances, and in particular by colloids. H. M. D.

Adsorptive Stratification in Gels. SAMUEL CLEMENT BRADFORD (*Biochem. J.*, 1916, **10**, 169—175).—The author brings forward evidence in favour of the view that the Liesegang phenomenon is due to gradual adsorption of the solute in the gel by the growing precipitate, so that, the adjacent layer of gel presently becoming exhausted of solute, the reacting substance is able to diffuse further into the gel before commencing to form a fresh stratum of precipitate. Working with a coloured solute, such as potassium chromate, in an agar gel and using lead nitrate as the precipitant, it is possible to observe the gradual exhaustion of the zone near the precipitate.

Stratification in agar gel occurs readily when potassium iodide and lead nitrate or manganese sulphate and liver of sulphur are the reacting substances, the strata being usually clearly defined provided the solutions are not too strong. In some cases better results are obtained when the reacting solutions are poured into the two limbs of a U-tube half filled with agar gel. After diffusing

through a column of gel in a U-tube the concentrations of the meeting solutions are reduced to the necessary dilution, whilst sufficient quantities of the reagents are available to produce well-defined disks.

The distances between the layers of precipitate are found to depend rather on the concentration of the solute in the gel than on that of the reagent penetrating from above. By interchanging the positions of the reacting substances, different intervals between the layers are obtained.

Experiments are also described in which silver nitrate and sodium chloride (which has a negative adsorption value) were the reacting substances. Stratification was not obtained in straight tubes, but when the solutions were placed in U-tubes containing agar gel, lamination was observed. Direct experiments to determine the nature of the adsorption of sodium chloride from solution by precipitated silver chloride indicated that the stratification in sodium chloride gels must be explained as the result of the negative adsorption.

Striking photographic illustrations of the strata obtained in various experiments are appended. H. W. B.

Adsorption of Narcotics by Gels. R. Somogyi (*Intern. Zeitsch. phys.-chem. Biol.*, 1916, **2**, 412—415).—The results of the experiments indicate that the amount of a narcotic, such as alcohol, acetone, or urethane, adsorbed by animal charcoal or by gelatinous silicic acid, does not bear any constant relation to its corresponding capillary-active power. H. W. B.

Temperature Effect in Dialysis and a Simple Rapid Dialyser. Marks Neidle (*J. Amer. Chem. Soc.*, 1916, **38**, 1270—1272).—It is pointed out that the rate of dialysis depends on (1) the nature of the membrane, (2) the area of the membrane in contact with liquid on both sides, (3) the difference in concentration of diffusible substances on the two sides of the membrane, and (4) the temperatures of the internal and external liquids. A rapid method of dialysis has been devised in which special advantage is taken of the third and fourth factors. It consists in suspending a parchment-paper membrane of about 1 litre capacity in a 2-litre beaker containing about a litre of the solution to be dialysed. Cold distilled water is run at a fairly constant rate into the membrane, which is kept rather more than half full by means of an automatic syphon. The colloidal solution in the beaker is heated to any desired temperature (70—90°). By means of such a dialyser a hydrous ferric oxide hydrosol can be prepared in twenty days which would require six months for its preparation by dialysis in the cold. E. G.

Demonstration of the Rational Character of New Formulæ of Solubility. Alb. Colson (*Compt. rend.*, 1916, **163**, 57—59).—A theoretical discussion from a thermodynamic point of view of formulæ recently propounded (compare this vol., ii, 374). W. G.

A Case of Elevation of Solubility. HANS VON EULER and ERIK LÖWENHAMN (*Zeitsch. Elektrochem.*, 1916, **22**, 199—200).—When benzoic acid and salicylic acid are simultaneously dissolved in water there is a mutual decrease in solubility which is in accord with the law of mass action. When these two acids are dissolved in a non-ionising solvent both acids become more soluble in the presence of the other; thus at 25° 100 c.c. of benzene solution contains 7·60 grams of benzoic acid and 0·762 gram of salicylic acid when the acids are taken alone, but when the acids are taken together 100 c.c. of solution contain 7·76 grams of benzoic acid and 2·50 grams of salicylic acid. The increase in solubility is held to be due to complex formation, of a weak kind, between the two acids. This idea is supported by cryoscopic measurements. J. F. S.

Protective Colloids. IV. Linseed as Protective Colloid. A. GUTBIER, J. HUBER and E. KUHN (*Kolloid. Zeitsch.*, 1916, **18**, 201—210. Compare this vol., ii, 231, 303).—The preparation of colloidal solutions from linseed is described. The seeds are shaken with water saturated with chloroform at the ordinary temperature for twenty-four hours and the aqueous extract subjected to dialysis either directly or after a preliminary purification by coagulation with alcohol.

The stability of the colloidal solutions has been examined with special reference to the influence of concentration, temperature, and electrolytes. H. M. D.

Agglutination of Colloidal Systems. T. MARUSAWA (*Intern. Zeitsch. phys.-chem. Biol.*, 1916, **2**, 430—443).—The rate of agglutination of various colloidal systems (arsenious sulphide, iron hydroxide, kaolin, charcoal, albumin, lecithin, blood serum, milk, and a bacterial emulsion) by acids, salts of the heavy metals, and dyes has been estimated by the author, who concludes that the agglutination is dependent chiefly on the potential (cohesion pressure) of the ions present (compare Traube, A., 1909, ii, 216). Electropositive systems are agglutinated most readily by acids such as tartaric and citric acids, whilst acids such as nitric and trichloroacetic acids are most effectual for the agglutination of electronegative systems. The rate of agglutination is dependent on two constants—the nature of the colloidal system and the agglutinating agent. Copper and lead are the most effective agglutinating agents, and the disinfecting power of their compounds is largely to be ascribed to the high irreversible agglutinating power of these cations. H. W. B.

Non-, Uni- and Bi-variant Equilibria. IX. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1676—1691. Compare this vol., ii, 381, 422).—In previous papers it has been shown that the types of pressure–temperature equilibrium diagrams may be derived without knowledge of the volume and entropy changes which are involved in the transformations associated with the invariant points. In order to obtain the direction of the equilibrium curves in the invariant point, the volume and entropy data are required. H. M. D.

Consecutive Reactions. I. The Measurement of Consecutive Reactions with a Single Set of Intermediate Products which can be Estimated Quantitatively. ANTON SKRABAL (*Monatsh.* 1916, **37**, 137—171).—It is shown that the velocity-coefficients characteristic of a reaction which takes place in two stages can be calculated from the experimental data, provided that the concentration of the intermediate substances as well as that of the reacting substances or final products can be determined at any particular moment by suitable analytical methods. An example of such a reaction is presented by the alcoholysis of the methyl ester of dioxalmalonic acid, which yields methyl malonate as a final product with the formation of monoxalmalonic ester as an intermediate step. In benzene solution the monoxalic derivative occurs almost exclusively in the enolic form, and may be estimated by Meyer's bromine method. H. M. D.

Halogen Oxy-compounds. XI. Kinetics of the Formation of Iodate from Hypoiodite for Small Iodide Concentrations. ANTON SKRABAL and RICHARD HOHLBAUM (*Monatsh.*, 1916, **37**, 191—203).—Further experiments on the rate of formation of iodate from hypoiodite in aqueous solution at 25° have shown that the velocity is independent of the concentration of the iodine ion when this falls below a certain small value. The limiting concentration varies with the hydroxyl-ion concentration of the solution. According to experiments in which the iodine-ion concentration was reduced to a very small value, which, moreover, remained unchanged throughout the course of the reaction, the velocity of the reaction is directly proportional to the square of the hypoiodite concentration and inversely proportional to the hydroxyl-ion concentration. The constant conditions referred to were attained by the addition of silver hydroxide to the solution, the mixture being thoroughly agitated during the course of the experiment to facilitate the removal of the iodine ion.

The reaction velocity was found to increase in the ratio 2·5/1 for a rise of 10°, and experiments in which varying quantities of sodium nitrate were added to the solution showed that the velocity is increased in presence of foreign electrolytes. H. M. D.

Time Reaction of the Neutralisation of Carbonic Acid and the True Dissociation Constant of Carbonic Acid. LOTTE PUSCH (*Zeitsch. Elektrochem.*, 1916, **22**, 206—212).—When carbonic acid is added to a solution of alkali coloured with phenolphthalein a short time elapses before the colour of the indicator entirely disappears. It has been shown that this slow disappearance of the colour is due to a time reaction. The nature of this reaction has been investigated in the present paper. The electrical conductivity of solutions of carbon dioxide and alkali was measured, and from the results it is decided that a time reaction occurs, namely, $OH' + CO_2 = HCO_3'$ (compare also A. Thiel, A., 1913, ii, 199). Measurements of the conductivity of solutions of carbonic acid show no change in the conductivity with time. This anomaly

is explained by the great acceleration of the reaction $HO' + CO_2 = HCO_3'$, by hydrogen ions. Similar catalytic action of the hydrogen ions is found in the transformation of γ-hydroxy-aliphatic acids into lactones and also in the inversion of sucrose. Conductivity measurements of mixtures of sodium hydroxide and carbonic acid show that the neutralisation takes place gradually. The equilibrium constant, calculated by the Thiel formula, is proportional to the concentration of the acid and the base, and inversely proportional to the quantity of hydrogen carbonate. At 0° it has the mean value 0·043. Experiments with ammonia, sulphurous acid, and acetic acid show no such behaviour; the neutralisation occurred instantaneously. By means of measurements of residual current the concentration of the undissociated carbonic acid was measured, and from this value the true dissociation constant calculated from $k_w = H^{\bullet} \times HCO_3'/H_2CO_3$. The value $7{\cdot}42 \times 10^{-4}$ was obtained. Comparative measurements were made with acetic acid, and from them it is shown that acetic acid has a smaller dissociation constant than carbonic acid. J. F. S.

Reaction between Iodic and Sulphurous Acids under the Influence of Catalysts of Biological Importance. L. BERCELLER (*Intern. Zeitsch. phys.-chem. Biol.*, 1916, **2**, 444—452).—The normal reaction is carried out as follows: 0·5 c.c. of sulphurous acid is added to a mixture of 5 c.c. of distilled water, 0·7 c.c. of a 0·202% solution of iodic acid, and 1 or 2 drops of a 0·5% starch solution. The concentration of the sulphurous acid is such that abou four minutes elapse before the blue colour suddenly appears. The author has now ascertained the effect on the rate of the reaction of replacing the 5 c.c. of distilled water with 5 c.c. of various solutions. The results may be summarised as follows: Acids accelerate, whilst alkalis inhibit the reaction; tartrates, sulphates, oxalates, and carbonates inhibit, whilst chlorides, bromides, and thiocyanates markedly accelerate the reaction. The cations do not, as a rule, have such a marked effect as the anions, but a trace of mercuric chloride strongly inhibits the reaction and so also do the corresponding bromide, iodide, and cyanide. Hydrocyanic acid also delays the reaction, and thus constitutes an exception to the general rule for acids. Most alkaloids lengthen the time of the reaction, but 2% of morphine reduces it by one-half. Colloids, such as proteins, colloidal silver or platinum, and lecithin delay the appearance of the blue colour; the alcohols and most dyes have a similar effect. A concentrated solution of sucrose accelerates, whilst a dilute solution inhibits the reaction. These substances, therefore, act as catalysts, and the changes they produce in the animal organism may, in part, be regarded as the outcome of the exercise of this catalytic function. H. W. B.

Catalytic Action of Palladium in Oxidation Reactions. G. SCAGLIARINI and G. B. BERTI-CERONI (*Gazzetta*, 1916, **46**, ii, 51—56).—At 110—120° the oxidation of oxalic acid by nitric acid is accelerated by the presence of a palladium salt, although not

to so marked a degree as by manganous (compare Villiers, A., 1897, ii, 492) or cerium salts (compare Barbieri and Volpino, A., 1907, ii, 465); the action consists apparently of alternate oxidations to palladic salt by the nitric acid and reductions to palladous salt by the oxalic acid. The oxidation of oxalic acid by persulphates is also accelerated by palladous chloride (compare Kempf, A., 1906, ii, 24). In presence of silver salts, persulphates oxidise ammonia in the cold and under suitable conditions the whole of the oxygen of the persulphate is used in oxidising the ammonia quantitatively to nitrogen (compare Marshall, A., 1901, ii, 156). The same results are obtained if the silver salt is replaced by a palladium salt, but in this case it becomes necessary to heat for some time to start the reaction.

Palladous salts readily undergo oxidation into palladic compounds, especially in the hot. Thus, when palladous nitrate solution is heated with concentrated ammonium or potassium persulphate, a brown, palladic compound, possibly Bellucci's hydrate (A., 1906, ii, 35) is deposited, which decomposes hydrogen peroxide and ammonia vigorously with liberation of gaseous products, and yields chlorine when heated with hydrochloric acid. Further, when a solution of potassium (or ammonium) palladochloride (or pallado-bromide) containing hydrochloric acid is heated with a persulphate, the corresponding palladichloride or palladibromide is precipitated on cooling. This reaction may be utilised in analysis when palladium is to be separated from a number of other elements.

T. H. P.

Catalytic Action of Dyes on the Formation of Colloidal Gold. I. TRAUBE and N. TAKAYASU (*Intern. Zeitsch. phys.-chem. Biol.*, 1916, **2**, 453—459).—The authors have investigated the influence of the addition of dyes on the separation of colloidal gold from a solution containing gold chloride and sulphurous acid, with and without the addition of iodic acid. Most of the dyes examined inhibit the reaction, particularly eosin, fluorescein, and other fluorescent dyes. Certain blue dyes, however, such as methylene-blue and isamine-blue, also malachite-green and acid violet, hasten the reaction. The dyes are regarded as functioning as catalysts, and in the case of the blue dyes their influence is perceptible even at a dilution of 1 in a thousand millions. H. W. B.

An Atomic Model. L. ZEHNDER (*Ber. Deut. physikal. Ges.*, 1916, **18**, 134—148).—In view of discrepancies between theory and experiment, the author is of the opinion that atomic models, which are based on the electron theory, are open to many objections. A model of an entirely different type is described, the properties of which are determined by its relation to the ether, which is assumed to be a substance with the attributes of other forms of matter.

In terms of this atomic model, it is said to be possible to explain the phenomena of light, electricity, and radioactivity. H. M. D.

A Hypothesis of Molecular Configuration in Three Dimensions of Space. SIR WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1916, [A], **92**, 451—462).—The views put forward in a previous paper (T., 1908, **93**, 781) have been elaborated, and an attempt is made to describe the mechanism which is involved in chemical combination.

It is supposed that the atom is spherical, and that the valency electrons revolve round this sphere forming a system which can be represented by a ball and a circular coil of wire through which a current is passed. Further assumptions made are (1) that the orbit is a circle the diameter of which is less than that of the sphere and is parallel to some equatorial plane which occupies a fixed position in the atom; (2) that the orbits of different valency electrons are not necessarily of the same diameter; and (3) that some electrons may revolve clockwise and others anti-clockwise, the direction being determined by the electro-positive or electro-negative character of the atom.

Models of such atoms have been constructed from very light and fairly rigid, hollow, celluloid spheres. Fine needles were attached to the ends of a diameter, and these were carefully centred so that the ball rotated on them as an axis. To represent an electron, a coil of silk-covered wire was glued to the side of the sphere at right angles to its equator, one end of the coil being attached to one needle and the other end to the opposite needle. By suitably pivoting the needles in cups containing liquid alloy, the balls are free to rotate about a vertical axis.

From experiments made with such atomic models, the conditions of stability for various systems of atoms have been determined, and these are described in detail. The combinations of spheres which have been submitted to examination were designed to throw light on the configuration of the molecules of hydrogen, oxygen, ozone, hydrogen chloride, water, hypochlorous acid, chlorine monoxide, and ammonia. H. M. D.

"Plate" Forms of Ultrafiltration Apparatus. GEORGE STANLEY WALPOLE (*Biochem. J.*, 1916, **10**, 254—262).—The author describes in detail two forms of "plate" ultrafiltration apparatus for use with the collodion membranes, the preparation of which has already been described (A., 1915, ii, 549). The membranes may also be prepared by Brown's method (A., 1915, ii, 824), and are to be preferred for close differentiation, as when, for instance, it is required to separate sugar from dextrin. Where, however, toxins or enzymes have to be freed from peptones or simpler substances, it is simpler to pour the film in the usual way and to plunge glass and membrane into water when drying has proceeded to the correct extent.

In the new apparatus the membranes are clamped between iron or aluminium plates, one of which has a corrugated (pyramidal pattern) surface. The solution for dialysis is forced under pressure to one side of the membrane and the dialysate flows away from the other. H. W. B.

Inorganic Chemistry.

An Active Modification of Nitrogen. VII. HON. R. J. STRUTT (*Proc. Roy. Soc.*, 1916, [A], **92**, 438—450. Compare A., 1915, ii, 336).—The circumstances in which active nitrogen is produced have been examined, the experiments being made with the steady discharge obtained from a direct current dynamo machine.

A comparison of the quantity of active nitrogen obtained from different parts of the discharge column has shown that this is greatest near the cathode, falls off to a minimum in the Faraday dark space, and increases again in the positive column to a value which is constant along that column, but is less than that in the neighbourhood of the cathode.

The results of experiments made with wide and with narrow discharge tubes show that, for the same current, much more active nitrogen is obtained from the positive column in the narrow tube. The difference in the yield cannot be accounted for by the difference in the potential gradients, for these are found to be very nearly equal, and it is supposed that the difference in yield is connected with the current density.

When the current of nitrogen is made to traverse varying lengths of the positive column it is found that the yield increases at first with the length of the column traversed, but that a limit is reached, and beyond this there is no appreciable increase in the yield of active nitrogen. This is shown to be due to the destructive action of the discharge, the active nitrogen being destroyed as fast as it is formed when a certain concentration has been attained.

Traces of oxygen and other gases have been found to increase largely the yield of active nitrogen. From experiments with nitrogen containing small amounts of oxygen, it appears that this quantity of oxygen increases considerably the fall of potential at the cathode, but has no measurable influence on the fall in the positive column.

Although the formation of active nitrogen is most easily demonstrated by experiments at low pressures, it can be shown that it is formed by sparking nitrogen at atmospheric pressure. The less striking character of the effects obtained at higher pressures is due to the more frequent collision of the active molecules with inert nitrogen molecules, whereby the active modification is destroyed.

If a stream of active nitrogen is made to pass over a copper cathode which is being scattered by the discharge, it is found that the luminous sheath exhibits the copper line spectrum. H. M. D.

The Rare Gases in Natural Gases. CHARLES MOUREU and ADOLPHE LEPAPE (*Ann. Chim.*, 1916, [ix], **5**, 225—257).—The conclusion of a résumé (compare this vol., ii, 389). W. G.

Allotropy and Solubilities in Water of Ammonium Bromide. ALEXANDER SMITH and HERBERT E. EASTLACK (*J. Amer. Chem. Soc.*, 1916, **38**, 1261—1266).—Scheffer (this vol., ii, 31) has shown by a study of the heating and cooling curves and the solubility between 160° and 205° that the enantiotropic transformation of ammonium chloride takes place at 184·5°.

Similar work has been carried out by the authors with ammonium bromide. The heating and cooling curves show that the transition point of this salt is between 130° and 143°. The solubilities in water have been determined by the closed tube method from 0° to 170°. A well-defined break in the solubility curve occurs at 137·3°, the transition temperature. The solubility (grams per 100 grams of water) increases from 60·6 at 0° to 99·2 at 50° and 145·6 at 100°. These results do not agree with the solubilities recorded by Eder (A., 1881, 683). E. G.

Ammoniates of Silver Salts. I. G. BRUNI and G. LEVI (*Gazzetta*, 1916, **46**, ii, 17—41).—The authors have made a systematic study of the ammoniates of inorganic and organic silver salts, the general method of preparation employed consisting in absorption of dry ammonia at different temperatures by the dry salt; in some cases ammoniacal-alcoholic solutions of the salt were precipitated by means of ether, and in others aqueous ammoniacal solutions of the salts were evaporated. The new compounds obtained are as follows:
$Ag_2O,2NH_3$; $AgF,2NH_3,2H_2O$ or $2AgF,4NH_3,5H_2O$; $AgClO_3,3NH_3$; $AgClO_4,2NH_3$ and $AgClO_4,3NH_3$; $AgClO_4,2NH_2Me$; $AgBrO_3,3NH_3$; $AgMnO_4,3NH_3$; $Ag_2SO_3,4NH_3$; $Ag_2SeO_3,4NH_4$; $AgCNO,2NH_3$; $H{\cdot}CO_2Ag,2NH_3$; $CO_2Ag{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Ag,4NH_3$;
$CO_2Ag{\cdot}CH{:}CH{\cdot}CO_2Ag$(fumarate)$,4NH_3$;
$CO_2Ag{\cdot}CH{:}C(CO_2Ag){\cdot}CH_2{\cdot}CO_2Ag,6NH_3$; $CN{\cdot}CH_2{\cdot}CO_2Ag,2NH_3$; $CHPh{:}CH{\cdot}CO_2Ag,2NH_3$; $C_6H_4(CO_2Ag)_2,4NH_3$; $C_6(CO_2Ag)_6,12NH_3$.
T. H. P.

Some Reactions of Calcium, Strontium, Zinc, and Magnesium Carbonates. W. ŒCHSNER DE CONINCK (*Ann. Chim. anal.*, 1916, **21**, 131—133).—Calcium carbonate reacts with potassium sulphate, potassium hydrogen sulphate, and potassium acetate when placed in contact with saturated solutions of these salts for several weeks, and calcium sulphate, or acetate, is found in the solution. Reaction takes place between strontium carbonate and saturated ammonium acetate solution, but reaction does not occur between potassium hydrogen sulphate and strontium carbonate and barium carbonate, respectively, under similar conditions. Barium carbonate is attacked slightly by potassium nitrate and ammonium chloride; the latter also decomposes magnesium carbonate. Zinc carbonate is strongly attacked by concentrated potassium hydrogen sulphate solution. W. P. S.

The Action of Carbon Dioxide at High Temperatures on Certain Metals and Metallic Compounds. FERRUCCIO VON BACHO (*Monatsh.*, 1916, **37**, 119—123).—Zinc sulphide, copper, and anti-

mony were heated in a porcelain tube placed in a resistance furnace, a current of carbon dioxide being passed through the tube.

Zinc sulphide begins to react at 750°, and at 1000° reaction takes place readily according to the equation $ZnS + 3CO_2 = ZnO + SO_2 + 3CO$. Metallic copper shows signs of reaction at its melting point (1070°), and at 1200° it is found that cuprous oxide and carbon monoxide are slowly formed. Antimony begins to react with carbon dioxide at about 830°, and at 1100° the reaction is found to occur in accordance with $2Sb + 3CO_2 = Sb_2O_3 + 3CO$. The antimony trioxide sublimes at this temperature. No evidence of the formation of higher oxides was obtained. H. M. D.

Equilibria of Mercuric Chloride with Other Chlorides. G. A. LINHART (*J. Amer. Chem. Soc.*, 1916, **38**, 1272—1280).—In an earlier paper (A., 1915, ii, 99) it has been shown that an aqueous solution of mercuric chloride contains two types of molecules, $HgCl_2$ and Hg_2Cl_4, which combine with sodium chloride to form complexes.

A study has now been made of the complex substances in solutions of sodium chloride and mercuric chloride by measurements of the distribution ratios of mercuric chloride between sodium chloride solutions and benzene. The results indicate that the only compounds existing in aqueous solutions are those which have already been prepared in solid, crystalline form. No complex mercuric chloride of sodium, potassium, or hydrogen has been shown to exist with a higher proportion of chloride than that of the type Na_2HgCl_4. In this connexion it is pointed out that, from a saturated solution of mercuric chloride and hydrogen chloride at −10°, Ditte was unable to obtain a compound richer in hydrogen chloride than HgH_2Cl_4. It is shown that the mention of the complex salt, HgH_3Cl_5, in Abegg's "Anorganische Chemie" is due to a misinterpretation of Ley's data. E. G.

Constitution of Manganic Compounds. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1916, **22**, 201—202).—Polemical. The author criticises several of the statements of Sem (A., 1915, ii, 777). It is pointed out that manganic salts exist in solutions of various colours, including violet, brown, red, dark green, and olive green, and not only in the first two, as stated by Sem. Further, the whole of these variously coloured solutions have practically identical absorption spectra. Consequently, Sem is not justified in subdividing manganic compounds into two classes from the difference of colour. It is further held to be unlikely that Sem obtained manganic nitrates by electrical oxidation. The brown product obtained is probably colloidal manganese peroxide. J. F. S.

The Polymorphic Transformations of Pure Iron. RUDOLF RUER and FRANZ GOERENS (*Ferrum*, 1915, **13**, 1—6).—Electrolytic iron, containing only 0·009% of carbon, is used for the determinations, after being melted in a porcelain tube in nitrogen. By means of a platinum-wound electric resistance furnace, thickly insulated

with asbestos, the rate of cooling over a given temperature interval may be varied within wide limits. In order to prevent oxidation, the mass of iron is enclosed in a porcelain test-tube and covered with broken porcelain to the top of the tube, and a slow stream of nitrogen is introduced by means of a gas-tight joint.

Such iron is found to freeze at 1528°, and to undergo the γ–δ-transformation at 1401°. The temperature of the β–γ-equilibrium is 906°, determined by comparing the heating and cooling curves at different rates. In the same way, the temperature of the α–β-equilibrium is determined to be 769°. There is no evidence of a change between 1000° and 1200°, the development of heat sometimes observed within that range being due to the presence of oxide. C. H. D.

Determination of the α–β-Transformation in Pure Carbon Steels by means of the Thermal Expansion. JOH. DRIESEN (*Ferrum*, 1915, **13**, 27—31).—On plotting the change of length for a given interval of temperature, $L_2 - L_1 / t_2 - t_1$, against the temperature, characteristic curves are obtained which are well suited to exhibit any discontinuities which may present themselves in the expansion of a steel. All the steels examined, ranging from 0·05 to 1·45% C., give an almost horizontal line at low temperatures, followed by a rapid fall, which reaches a minimum at 745°. This corresponds with the conversion of the pearlite into a solid solution. The steels containing less than 0·40% C. then exhibit a well defined maximum at 765—775%, corresponding with the α–β-transformation. The maximum which follows indicates the beginning of the β–γ change. Steels containing more than 0·4% C. give curves with only a single depression, due to the pearlite change. C. H. D.

Reactions between Ferrous Oxide and Carbon and between Carbon Monoxide and Iron. V. FALCKE (*Zeitsch. Elektrochem.*, 1916, **22**, 121—133. Compare A., 1915, ii, 169).—A continuation of experiments already described (*loc. cit.*). A number of experiments are made with the object of directly comparing the author's values with those of Schenk (A., 1905, ii, 519; 1907, ii, 470). J. F. S.

Constitution of Chromic Acid. I. ASWINI KUMAR DATTA and NILRATAN DHAR (*J. Amer. Chem. Soc.*, 1916, **38**, 1303—1308).—In view of the different opinions which have been expressed with regard to the question whether chromic acid should be represented as H_2CrO_4 or $H_2Cr_2O_7$, a study has been made of the molecular solution volumes and molecular refractivities of chromic acid, potassium chromate, and potassium dichromate. The results in each case are in support of the formula $H_2Cr_2O_7$. E. G.

The Atomic Weight of Uranium. OTTO HÖNIGSCHMID and STEFANIE HOROVITZ (*Monatsh.*, 1916, **37**, 185—190).—Hitherto all atomic weight determinations of uranium have been on material separated either from Joachimsthal or Cornish pitchblende. The

present determination is for uranium separated from Morogoro (German E. Africa) crystallised uranium mineral, which is almost free from impurities, and, from the Pb : U ratio, is about 800 million years old, as compared with about 250 million years for pitchblende. The latter contains as impurities nearly all the known elements. Two series of determinations, the first with uranous bromide sublimed finally in bromine vapour, and the second in nitrogen, were made, as in the earlier revision of the atomic weight of uranium from pitchblende (Hönigschmid, A., 1914, ii, 662), to give minimum and maximum values respectively. The mean results were 238·043 ± 0·018 and 238·159 ± 0·023. The latter agrees with the value 238·175 before found, within the limit of experimental error. In the second series, in five analyses, 24·09148 grams of uranium tetrabromide required 18·63650 grams of silver and gave 32·44272 grams of silver bromide (Ag = 107·88 ; Br = 79·916).

F. S.

Peptisation of Solid Thorium Oxide. V. KOHLSCHÜTTER and A. FREY (*Zeitsch. Elektrochem.*, 1916, **22**, 145—161).—Thorium dioxide, prepared by the ignition of thorium nitrate, sulphate, or hydroxide, is not attacked by acids, whereas that prepared by ignition of the oxalate forms a colloidal solution in water after treatment with acid. The latter form of thorium dioxide differs from the former in most of its specific reactions. The present paper deals with the connexion between the mode of formation and that of peptisation of the solid oxide. The condition necessary for the production of an oxide which may be completely dissolved to a colloidal solution is that the temperature of ignition of the oxalate must not exceed 700°, and the product thus produced must not be kept at temperatures above 500° for any considerable time. In this way a loose, fine, white, anhydrous oxide is obtained which readily absorbs small quantities of carbon dioxide and aqueous vapour from the air and at the same time loses its colloidal properties. The colloidal properties may, however, be regenerated by heating gently for a short time. Peptisation of thorium dioxide is effected by means of nitric, hydrochloric, hydrobromic, hydriodic, and sulphuric acids, and by easily hydrolysed salts of these acids. An elevation of the temperature accelerates the change, and concentrated solutions work more rapidly than dilute solutions. A definite quantity of acid is required to peptise a given quantity of thorium dioxide. The minimum relationship, acid/oxide, increases with decreasing concentration of the acid, and also with increasing amount of the oxide. Peptisation is accompanied by a decrease in the volume of the colloidal system, which is probably to be explained by the porous nature of the solid oxide. During peptisation the electrical conductivity and the titre of the acid decrease, and the presence of thorium salts in the solution can be proved analytically, but peptisation and solution do not proceed parallel to one another. Thorium dioxide sols are turbid and opalescent even at high dilution. They are very sensitive to the presence of electrolytes. Sols prepared from solid thorium dioxide differ both in appearance and

in their general behaviour from those prepared from freshly precipitated thorium hydroxide. The viscosity of the solvent is slightly increased by the colloidal substance and the particles are positively charged. The sols are very stable both with regard to temperature and time. On evaporation of sols, solid gels are produced which dissolve spontaneously in water and may be submitted to high temperatures without losing their great solubility. The peptisation of thorium dioxide may be explained as follows: The acid reacts with the surface layer of the oxide particles, and thereby produces ions of either $Tl^{\cdot\cdot\cdot\cdot}$ or $ThO_2^{\cdot\cdot}$, which become either directly or indirectly a constituent part of the sol particles and furnish the necessary electric charge. Colloidal thorium dioxide is therefore to be regarded as the first step on the way from solid thorium dioxide to a dissolved thorium compound. J. F. S.

Occurrence of Germanium in Zinc Materials. G. H. BUCHANAN (*J. Ind. Eng. Chem.*, 1916, **8**, 585—586).—A by-product derived from Wisconsin blende (the exact nature of this product cannot at present be disclosed) contained 0·25% of germanium oxide; a few other zinc ores, including some from Mexico, were also found to contain germanium, but in very small quantity. W. P. S.

The Doubly-refractive Sol of Vanadium Pentoxide. H. R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 1625—1631. Compare Dieselhorst and Freundlich, this vol., ii, 65). —The appearance presented by a colloidal solution of vanadium pentoxide, when examined by the ultramicroscope, is described in detail. When a cardioid-ultramicroscope is used, the interference images show the presence of very elongated rod-like structures in quiet Brownian motion, together with small, round disks in a state of rapid movement. Some of the rods form combinations of varying degrees of complexity, the larger aggregates depositing as flakes. With a slit-ultramicroscope, it was found that the elongated particles can only be seen when their axes deviate by less than 30° from a line perpendicular to the axis of the illuminating beam.

The effects produced by the action of an electric field are also described. When the field is parallel to the direction of the luminous beam, very little dispersion takes place, and the elongated particles apparently disappear. On the other hand, when the field is perpendicular to the luminous beam, the Tyndall effect is very pronounced.

The observations are in agreement with the view that the vanadium pentoxide sol is in many respects very closely similar to a liquid crystal. H. M. D.

Mineralogical Chemistry.

Hydrozincite. W. E. FORD and W. A. BRADLEY (*Amer. J. Sci.*, 1916, [iv], **42**, 59—62).—Radiating masses of small crystals of hydrozincite occur in crevices in massive calamine ($ZnCO_3$) at Good Springs, Lincoln Co., Nevada. The crystals are very thin, platy or lath-shaped, and have a pearly lustre. They are optically biaxial and negative; $\alpha=1\cdot650$, $\gamma=1\cdot740$. Analysis I of the crystals and II of the underlying crystalline mass. For comparison, anal. III of massive hydrozincite from Malfidano, Sardinia.

	ZnO.	H_2O.	CO_2.
I.	75·58	8·64	[15·78]
II.	74·67	8·92	[16·41]
III.	73·72	10·81	[15·47]

These analyses, as well as the average of twenty-seven previously published analyses, agree with the formula $2ZnCO_3,3Zn(OH)_2$. Aurichalcite has a similar formula, but differs in containing about 20% of cupric oxide, replacing zinc oxide; moreover, the optical characters, so far as determined, are in agreement, and it is suggested that these minerals belong to practically the same species.

L. J. S.

Analytical Chemistry.

Estimation of Dissolved Oxygen in Polluted Waters. L. W. WINKLER (*Zeitsch. Nahr. Genussm.*, 1915, **29**, 121—128).—Waters containing nitrites and organic matter are treated with calcium hypochlorite solution (containing sodium sulphate to increase its specific gravity) and dilute sulphuric acid; the excess of chlorine is then destroyed by the addition of potassium thiocyanate, and the oxygen is estimated in the usual way; manganous sulphate is used in place of manganous chloride, and sulphuric acid instead of hydrochloric acid for acidifying the final solution. In the case of waste waters containing large quantities of organic substances, the dissolved oxygen must be estimated gasometrically.

W. P. S.

Identification of Water which has been Treated with Alkaline Hypochlorites. CH. GUILLAUMIN (*Ann. Chim. anal.*, 1916, **21**, 137; from *Soc. Pharm.*, 1915).—Nitrites are absent from water which has been treated with alkaline hypochlorites, and the quantity of chlorine absorbed by a water under definite conditions is diminished when the water has been treated previously with hypochlorite. W. P. S.

States of Combination of Sulphur in Wine and their Estimation. W. J. BARAGIOLA and O. SCHUPPLI (*Zeitsch. Nahr. Genussm.*, 1915, **29**, 193—221).—Sulphur occurs in wine principally as inorganic and organic sulphates; free and combined sulphurous acid, and "neutral" sulphur (sometimes called protein sulphur), are also present. A small quantity of free sulphur (partly colloidal) is found in some wines. Inorganic sulphuric acid is estimated by precipitation in the cold with barium chloride in an atmosphere of carbon dioxide; the organic sulphuric acid is estimated by heating the filtrate from the barium sulphate precipitate. Von der Heide's method (A., 1913, ii, 722) is trustworthy for the estimation of the total sulphuric acid. Wines contain only traces, if any, of sulphuric acid in organic combination. The total sulphurous acid is estimated by distillation in the presence of phosphoric acid, whilst Mathieu and Billon's method may be used for the estimation of the combined sulphurous acid (oxidation of the free sulphurous acid by a slight excess of iodine, adding an excess of sodium arsenite, and distilling the combined sulphurous acid after this has been liberated by phosphoric acid). For the estimation of total sulphur the wine is treated with sodium carbonate and hydrogen peroxide, evaporated to dryness, the residue mixed with potassium nitrate, and ignited; the sulphate in the ash is then estimated gravimetrically. "Neutral" sulphur is estimated by boiling the wine with hydrochloric acid to expel sulphur dioxide, precipitating the sulphuric acid with barium chloride, oxidising the filtrate from the barium sulphate with nitric acid, and precipitating the resulting sulphuric acid with barium chloride. W. P. S.

Separation and Estimation of Polysulphides and Thiosulphate in Lime-Sulphur Liquors. S. D. AVERITT (*J. Ind. Eng. Chem.*, 1916, **8**, 623—627).—Calcium polysulphide may be decomposed by iodine solution, and thus eliminated from a solution containing thiosulphate previous to the titration of the latter. As applied to lime-sulphur liquors the method depending on this fact is carried out as follows: An aliquot portion of the diluted lime-sulphur liquor is titrated with $N/10$-iodine solution until the yellow colour has nearly disappeared; a small crystal of sodium nitroprusside is then added, and the iodine solution is run in until the purple coloration is discharged. The titration with the iodine solution is then continued to obtain the amount of thiosulphate present. Hydrochloric acid may be used to decompose the polysulphide, but in this case the hydrogen sulphide must be expelled by boiling the solution before the thiosulphate is titrated. The author has established the fact that hydrogen sulphide may thus be expelled without decomposing the thiosulphate. An alternative method consists in adding iodine solution until both the sulphide and thiosulphate have been decomposed; one drop of ammonia and a slight excess of sodium sulphide solution are then added, the mixture rendered slightly acid with hydrochloric acid, the hydrogen sulphide expelled by boiling, and the solution titrated with iodine solution. This method depends on the fact that sodium sulphide

reacts with tetrathionate to form thiosulphate, the tetrathionate being formed by the action of the iodine on the thiosulphate present originally. A fourth method consists in separating the sulphide by means of ammoniacal cadmium chloride solution before the thiosulphate is titrated with iodine solution. All four methods yield trustworthy results. The sulphur precipitated when the solution is treated by iodine solution or hydrochloric acid may be collected on a weighed filter, washed, dried at 96° for forty-five minutes, and weighed. W. P. S.

Rate of Distillation of Ammonia from Water. F. W. BRUCKMILLER (*J. Ind. Eng. Chem.*, 1916, **8**, 602—603).—For all practical purposes it is not necessary to collect and nesslerise more than three 50 c.c. portions of distillate for the estimation of free ammonia in waters, and four 50 c.c. portions for the albuminoid ammonia. The error will not amount to more than 0·05 part of ammonia per million of water in the case of free ammonia or more than 0·2 part of albuminoid ammonia. W. P. S.

Sodium Sulphate as a Substitute for Potassium Sulphate in the Gunning Modifications for the Estimation of Nitrogen. W. L. LATSHAW (*J. Ind. Eng. Chem.*, 1916, **8**, 586—587).—Anhydrous sodium sulphate is an efficient substitute for potassium sulphate in the estimation of nitrogen by the Kjeldahl-Gunning method; about 7 grams of the salt should be used in each estimation. W. P. S.

Kjeldahl Modification for the Estimation of Nitrogen in Nitro-substitution Compounds. W. C. COPE (*J. Ind. Eng. Chem.*, 1916, **8**, 592—593).—The nitrogen in such substances as nitrotoluenes, nitrobenzenes, picric acid, etc., may be estimated as follows: About 0·5 gram of the substance is dissolved in 30 c.c. of sulphuric acid containing 2 grams of salicylic acid; the cold mixture is then treated with 2 grams of zinc dust, added in small portions at a time, and after two hours the mixture is boiled for two hours. The boiling is continued for one hour after the addition of 1 gram of mercuric oxide, the mixture then cooled, 7·5 grams of potassium sulphate and 10 c.c. of sulphuric acid are added, and the mixture is boiled for two hours. The ammonia is now distilled in the usual way. W. P. S.

Estimation of Total Nitrogen in Urine. R. DHOMMÉE (*Ann. Chim. anal.*, 1916, **21**, 135—137; from *Bull. Sci. pharm.*, 1915).—Ten c.c. of the urine are heated in a flask with 5 c.c. of 40% sodium hypophosphite solution and 10 c.c. of concentrated sulphuric acid until the organic matter has been destroyed; the clear liquid is then neutralised with sodium hydroxide solution, using phenolphthalein as indicator; 40 c.c. of neutral 35% formaldehyde solution are added, and the mixture is titrated with $N/10$-sodium hydroxide solution. The number of c.c. of the latter solution used is multiplied by 0·1446 to obtain the weight of total nitrogen per litre of urine. W. P. S.

Detection and Estimation of Nitrates in Waters. L. W WINKLER (*Zeitsch. Nahr. Genussm.*, 1915, **29**, 10—17).—One hundred c.c. of the water are treated with starch solution and potassium iodide and then acidified with phosphoric acid; a blue coloration appears at once if the water contains 0·5 mg. or more of N_2O_3 per litre, whilst 0·05 mg. of N_2O_3 yields a blue coloration after the lapse of about ten minutes. In the case of waters containing less than 0·3 mg. of N_2O_3 per litre, the quantity of the latter may be estimated by placing 100 c.c. of the sample (previously shaken in contact with air) in a stoppered flask, adding starch solution and 0·2 gram of potassium iodide, and acidifying the mixture with 5 c.c. of 25% phosphoric acid. The flask is placed in the dark for twenty-four hours, and the liberated iodine then titrated with *N*/200-thiosulphate solution. Owing to secondary reactions which take place, the quantity of thiosulphate used is not strictly proportional to the amount of nitrous acid present; a table is given showing the value of the thiosulphate solution in terms of nitrous acid. For the estimation of larger quantities of nitrous acid, 100 c.c. of the water are acidified with phosphoric acid, starch solution and 5 grams of potassium hydrogen carbonate are added, followed, after a short time, by 0·2 gram of potassium iodide, and, after ten minutes, the iodine is titrated with thiosulphate solution. Ferrous salts, if present, must be removed from the water previously by treatment with sodium hydroxide and filtration.

W. P. S.

Titration of Hypophosphites. J. M. KOLTHOFF (*Pharm. Weekblad*, 1916, **53**, 909—916).—Solutions of hypophosphites can be accuratelv estimated by oxidation with permanganate, iodine, chlorine, or bromine. Satisfactory results are not obtained with hydrogen peroxide, potassium percarbonate, or potassium persulphate.

A. J. W.

Grete's Direct Volumetric Method for Estimating Phosphoric Acid in Manures. GEORG INCZE (*Landw. Versuchs-Stat.*, 1916, **88**, 433—444).—A description of Grete's method (A., 1888, 1341; 1909, ii, 936), in which a solution of glue (prepared by boiling ordinary glue with nitric acid and afterwards freeing the solution from phosphoric acid and calcium) is employed as indicator. The method, which yields satisfactory results, requires, at first, a good deal of patience. The solutions must be free from hydrochloric acid and organic matter, and must not contain at all large amounts of iron.

N. H. J. M.

Recovery of Ammonium Molybdate from the Filtrates obtained in the Estimation of Phosphorus in Steel and Iron. RICHARD FRIEDRICH (*Chem. Zeit.*, 1916, **40**, 560—561).—The filtrates are treated with sodium phosphate, the yellow precipitate of ammonium phosphomolybdate is collected, washed with water containing sodium sulphate, and air-dried. Five hundred grams of the dry precipitate are then dissolved in concentrated ammonia,

and the solution is treated with 30 grams of ammonium chloride and 60 grams of magnesium chloride; the ammonium magnesium phosphate is separated by filtration, dissolved in hydrochloric acid, and any ammonium phosphomolybdate which may be precipitated is collected. The filtrate from the ammonium magnesium phosphate precipitate is treated with a few drops of hydrogen peroxide solution, and hydrochloric acid is added until molybdic acid is no longer precipitated; an excess of hydrochloric acid is to be avoided. The precipitated molybdic acid is collected, washed, dried, and dissolved in ammonia (1 : 1) at 90°; the solution, on cooling, deposits crystalline ammonium molybdate. The mother liquor from these crystals and the filtrate from the molybdic acid precipitate are added to subsequent filtrates from which molybdic acid is to be recovered. W. P. S.

The Silver Arsenate Test for Arsenic. L. J. Curtman and P. Daschavsky (*J. Amer. Chem. Soc.*, 1916, **38**, 1280—1282).—The test in which arsenic is precipitated in the form of silver arsenate has been studied with the object of ascertaining the conditions in which it will give constant results. It has been found that with solutions of pure sodium arsenate the addition of silver nitrate is capable of detecting 0·02 mg. of arsenic. In presence of ammonium nitrate, 0·2 mg. of arsenic in the form of sodium arsenate can be detected. In systematic analysis, 0·5 mg. of arsenic can be detected with certainty by means of the following procedure.

The solution (20 c.c.) containing one or more of the elements, arsenic, antimony, and tin, is neutralised with ammonia, 2·5 c.c. of concentrated hydrochloric acid are added, and the mixture is heated until it boils, and then treated with hydrogen sulphide. The solution is diluted to 100 c.c. and again treated with hydrogen sulphide until precipitation is complete. The precipitate is collected, transferred to a beaker, heated for five minutes with 10 c.c. of concentrated hydrochloric acid, and the product is diluted and filtered. The residue is washed and boiled with 2 c.c. of concentrated nitric acid, and the solution is filtered. The filter-paper is washed, and the filtrate and washings are concentrated to 2 c.c. and transferred to a test-tube. Silver nitrate is added, the solution is rendered slightly alkaline with ammonia, and then acidified faintly with acetic acid and left for a few minutes. E. G.

Estimation of Total Carbon in Soils. Robert M. Salter (*J. Ind. Eng. Chem.*, 1916, **8**, 637—639).—The method described depends on the combustion of the soil in oxygen, the resulting gases being dried over phosphoric oxide and then absorbed in a soda–lime tube. The gases are passed over granulated zinc before entering the drying and absorption tubes, in order to remove sulphur, chlorine, or acid fumes. A convenient form of apparatus for use in the estimation is illustrated; a three-way tap at the exit end of the combustion tube enables a current of oxygen to be drawn through the tube, previous to the estimation, without allowing it to pass through the absorption part of the apparatus.

W. P. S.

Modification of the Gas Burette of the Parr Total Carbon Apparatus. HOWARD LOOMIS (*J. Ind. Eng. Chem.*, 1916, **8**, 639). —It sometimes happens that, after the absorption of the carbon dioxide, the volume of the residual air is less than 100 c.c. and cannot be measured directly in the burette. A second three-way tap is therefore inserted between the generating flask and the burette, so that a measured volume of air can be admitted to the burette. The residual air from the absorption pipette is then forced into the burette and its volume measured by difference.

W. P. S.

Estimation of Potassium in Potassium Salts by the Perchlorate Method. B. SCHULZE (*Landw. Versuchs-Stat.*, 1916, **88**, 397—398).—A reply to Hager and Kern (this vol., ii, 114). The loss of potassium in barium sulphate precipitates has long been known (Fresenius's "Lehrbuch," **1**, 151), but has been overlooked. This source of error is of importance in the case of salts containing small amounts of potassium and large amounts of sulphates.

N. H. J. M.

Estimation of Calcium. EDWARD CAHEN and WILLIAM HOLDSWORTH HURTLEY (*Biochem. J.*, 1916, **10**, 308—312).—The method is devised to estimate the calcium in tissues which on incineration yield a residue which is only dissolved in sulphuric acid with great difficulty. It is found that such a calcined residue dissolves completely and immediately when heated with a solution of phosphoric acid of suitable strength.

The tissue (100 grams) is dried and incinerated in the usual way. To the residue 10—20 c.c. of phosphoric acid (D 1·2) (1 vol. of syrupy phosphoric acid to 3 vols. of water) are added, and heat is gently applied. The residue dissolves readily, and after diluting with 50—100 c.c. of water a large excess of a 3·78% solution of crystallised oxalic acid is added. Precipitation is rapid, and the precipitate is crystalline, but a little calcium remains in solution. To effect complete precipitation a volume of ammonia equal to that of the oxalic acid used is then added, the strength of the ammonia being exactly equivalent to that of the oxalic acid, namely, 1·02% NH_3. If magnesium is present, the ammonia must be added slowly from a burette, with shaking. After one hour, the solution filters quickly, and the filtrate is perfectly clear. The calcium is then estimated gravimetrically, or volumetrically with permanganate, in the usual way.

When excess of magnesium is present, a little of it may be precipitated with the calcium oxalate. It is, in this case, advisable to redissolve the calcium oxalate precipitate in phosphoric acid and reprecipitate as oxalate.

H. W. B.

Modification of McCrudden's Method for Calcium, for the Estimation of Calcium and Strontium in the Presence of Phosphoric Acid and a Small Amount of Iron. O. B. WINTER (*J. Ind. Eng. Chem.*, 1916, **8**, 603—604).—The following

modification of the method (A., 1910, ii, 243) yields trustworthy results: The solution containing calcium and strontium is diluted to 200 c.c., a few drops of alizarin solution are added, followed by ammonia, until the solution is just alkaline; the solution is then rendered slightly acid with hydrochloric acid, 10 c.c. of $N/2$-hydrochloric acid and 10 c.c. of 2·5% oxalic acid solution are added, the mixture is boiled, and saturated ammonium oxalate is introduced in small quantities at a time until about twice the amount required to precipitate the calcium and strontium has been added. When cold, the mixture is treated with 8 c.c. of 20% sodium acetate solution and 15 c.c. of 95% alcohol; the presence of the latter insures the complete precipitation of the strontium oxalate. After sixteen hours the precipitate is collected, washed with 1% ammonium oxalate solution containing 20% of its volume of alcohol, ignited, the resulting oxides are dissolved in nitric acid, the solution is evaporated, and the calcium nitrate separated from the strontium nitrate by means of absolute alcohol and ether. W. P. S.

Bottle for the Iodometric Titration of Copper. O. Dexter Neal (*J. Amer. Chem. Soc.*, 1916, **38**, 1308—1309).—The use of potassium iodate for iodometric estimations as described by Andrews (A., 1903, ii, 686) has been applied by Jamieson, Levy, and Wells (A., 1908, ii, 634) to the estimation of copper in ores. Hydrogen cyanide is liberated in this process with development of sufficient pressure to cause the ejection of particles of liquid when the stopper is removed from the bottle during the addition of successive quantities of the iodate solution. The use of an open flask does not admit of sufficient freedom in shaking, but the difficulty can be overcome by replacing the glass stopper by a two-holed rubber stopper carrying two glass tubes about 8 cm. long, one widened at the top for the introduction of the iodate solution and the other serving as an outlet for the vapour, their length preventing loss of liquid during shaking. A more efficient form is described, which consists of a bottle with a one-holed rubber stopper through which passes a tube, 7—8 mm. in diameter, widened at the upper end and narrowed and curved at the lower end, and provided with an aperture just below the stopper. This aperture serves for the escape of gases and also enables the last drop of iodate solution to be washed down by shaking the bottle. This bottle has been found quite satisfactory in practice. E. G.

Estimation of Aluminium as Oxide. William Blum (*J. Amer. Chem. Soc.*, 1916, **38**, 1282—1297).—The various recommendations which have been made from time to time in connexion with the estimation of aluminium by precipitation with ammonium hydroxide and subsequent ignition to the oxide, have been considered and the best conditions for the estimation have been established. Observations made with the hydrogen electrode as suggested by Hildebrand and Harned (A., 1913, ii, 727) showed that the precipitation of aluminium hydroxide by ammonia is complete when $[H^+]=10^{-6\cdot5}$ to $10^{-7\cdot5}$, points which are defined approxi-

mately by the colour change of methyl-red and of rosolic acid. The presence of ammonium chloride during precipitation is of advantage in limiting the alkalinity and coagulating the precipitate. Solutions of ammonium nitrate and ammonium chloride are equally satisfactory for washing the precipitate. Owing to the hygroscopic nature of aluminium oxide, crucibles containing it should be kept covered in the desiccator and on the balance. The presence of aluminium chloride during ignition does not cause any appreciable loss of aluminium oxide.

The following procedure is recommended. To the solution, containing at least 5 grams of ammonium chloride (or an equivalent amount of hydrochloric acid) a few drops of methyl-red (0·2 alcoholic solution) are added, and the solution is heated until it boils. Dilute ammonium hydroxide is added drop by drop until the solution becomes yellow. The solution is then boiled for one to two minutes and filtered. The precipitate is washed with hot 2% solution of ammonium chloride or nitrate, and is then ignited in a platinum crucible until all the carbon has been burned off, and is afterwards heated for five minutes with the blowpipe. The crucible is allowed to cool in a desiccator and weighed. It is advisable to heat a second time with the blow-pipe for five minutes and re-weigh. E. G.

Electroanalysis of Cobalt Without Platinum Electrodes. J. Guzmán Carrancio and E. Jimeno (*Anal. Fis. Quim.*, 1916, **14**, 250—257).—An account of the application of Guzmán's electrolytic method with a cathode of copper and an anode of passive iron to the separation of copper from cobalt and from nickel. A. J. W.

Qualitative and Quantitative Analysis of Tungsten. M. L. Hartman (*Chem. News*, 1916, **114**, 27—28; from *Pahasapa Quarterly*).—Tungsten may be identified by the blue coloration which is obtained when a substance (ore) containing the metal is fused with sodium carbonate and the mass then treated with hydrochloric acid and zinc. Under similar conditions, columbium gives a blue coloration, which disappears when the mixture is diluted with water; vanadium salts also give a blue coloration when reduced, but tartaric acid will effect this reduction whilst it will not reduce tungsten salts. Three methods are available for the estimation of tungsten. *Hydrofluoric Acid Method.*—The powdered ore is digested for several hours on a water-bath with a mixture of hydrochloric and hydrofluoric acids, and the solution then evaporated with an excess of hydrochloric acid to a volume of about 15 c.c. Twenty c.c. of hydrochloric acid and 8 c.c. of nitric acid are now added, the mixture evaporated to about 10 c.c., diluted with 50 c.c. of hot water, boiled for thirty minutes, and the precipitated tungstic acid is collected on a filter and washed with very dilute hydrochloric acid. The precipitate is then dissolved in ammonia, the solution evaporated to dryness, the residue ignited, and weighed as WO_3. *Fusion Method.*—The ore is fused with a mixture of sodium and potassium carbonates, and the aqueous solution of the

alkali tungstate is evaporated with nitric acid; the residue thus obtained is heated at 120°, moistened with nitric acid, ammonium nitrate solution is added, and the precipitate collected, washed with ammonium nitrate solution, dried, and ignited. Silica is removed from the ignited precipitate by treatment with hydrofluoric acid, and stannic oxide may be volatilised by heating the precipitate with ammonium chloride. *Aqua Regia Method.*—The ore is heated with about 50 c.c. of *aqua regia*, and when the solution has evaporated to 10 c.c., 50 c.c. of hot water are added. After thirty minutes the liquid is poured through a filter, the insoluble portion washed by decantation, then treated with ammonia, the ammoniacal solution filtered, evaporated to dryness, and the residue ignited. The latter may be treated with hydrofluoric acid to remove remaining traces of silica. W. P. S.

Reduction Test for Tungsten. M. L. HARTMAN (*Chem. News*, 1916, **114**, 45—46; from *Pahasapa Quarterly*).—The following is the best way of carrying out the reduction test for tungsten. About 0·5 gram of the ore is fused with 4 grams of sodium carbonate, the cooled mass dissolved in a small quantity of hot water, the solution acidified with hydrochloric acid, and treated with a piece of tin. A blue coloration indicates the presence of tungsten. Zinc may be used in place of tin, but in this case it is necessary to warm the solution to obtain the reduction (blue coloration). If the reduction proceeds at the ordinary temperature for two days, the blue colour changes to brown. Hydrogen peroxide and oxalic acid do not reduce tungstic acid. (See preceding abstract for the colorations given by other metals under similar conditions.) W. P. S.

Separation of Thorium from Iron with the Aid of the Ammonium Salt of Nitrosophenylhydroxylamine ("Cupferron"). WILLIAM M. THORNTON, jun. (*Chem. News*, 1916, **114**, 13—14; *Amer. J. Sci.*, 1916, [iv], **42**, 151—154).—Whilst the presence of sulphuric acid is essential to the complete precipitation of zirconium by "cupferron" (compare A., 1914, ii, 779), thorium can be precipitated completely only from an acetic acid solution; the precipitate formed is collected, washed with 1% ammonium acetate solution, dried, and ignited to thorium oxide. Separation of thorium from iron may be effected by means of "cupferron," but it is not suggested that it will replace the well-known oxalic acid method.

W. P. S.

Estimation of Vanadic Acid after Reduction by Metallic Silver. GRAHAM EDGAR (*J. Amer. Chem. Soc.*, 1916, **38**, 1297—1302).—Experiments are described which show that vanadium can be quantitatively reduced by silver from the quinquevalent to the quadrivalent condition. Measured volumes of a standard solution of sodium vanadate (equivalent to about 0·1 gram V_2O_3) were acidified with 2 c.c. of concentrated sulphuric acid, diluted to about 75 c.c., and boiled with a weighed quantity (1—2 grams) of silver for twenty to thirty minutes. In each experi-

ment the solution was filtered through asbestos in a perforated porcelain crucible, and the residue of silver washed with hot water. The crucible was heated to a very low red heat, cooled in a desiccator, and weighed, and the loss of silver was calculated. The filtrate containing the vanadium in the quadrivalent state, together with the dissolved silver, was titrated while hot with 0·05*N*-potassium permanganate, and after this titration had been completed the solution was cooled and titrated for silver with 0·05*N*-ammonium thiocyanate after the addition of ferric alum as indicator. The amount of vanadic acid present was calculated (1) from the weight of silver, (2) from the permanganate titration, and (3) from the amount of silver equivalent to the quantity of ammonium thiocyanate used. The results show that vanadic acid can be accurately estimated gravimetrically from the loss in weight of the silver or volumetrically by titration with potassium permanganate or ammonium thiocyanate after reduction with silver.

The reaction may also be applied to the standardisation of permanganate solutions against silver or of permanganate and thiocyanate solutions against each other. E. G.

The Quantitative Analysis of Antimony Trisulphide and the Products Obtained from it by Roasting. FERRUCCIO VON BACHO (*Monatsh.*, 1916, **37**, 85—117).—Apropos of an investigation of the products formed in the roasting of antimony trisulphide, the various methods employed in the estimation of antimony, sulphur, and the oxidation products have been submitted to a critical examination. For the experiments on the estimation of sulphur, a pure sample of precipitated antimony trisulphide was employed. This was decomposed by boiling with 25% hydrochloric acid in an atmosphere of hydrogen and the hydrogen sulphide evolved absorbed by one or other of various reagents. From experiments made with ammoniacal solutions of cadmium sulphate, alkaline and ammoniacal solutions of arsenious oxide, sodium hydroxide solutions, and ammoniacal and alkaline solutions of copper sulphate, it has been found that the best results are obtained when a 3—4% solution of sodium hydroxide is used for the absorption of the hydrogen sulphide. All the solutions should be air-free, and the alkaline sulphide solution should be added slowly, under continuous stirring, to an acidified solution of iodine, the strength of which should not exceed *N*/100.

The bromate and iodine methods for the estimation of antimony are found to give consistent results, but in both cases the quantities found by experiment are about 1% smaller than the theoretical amounts. This is in agreement with previous analytical experience, and since both methods yield results in agreement with theory if the older value of 122·0 is taken for the atomic weight of antimony, it is suggested that the atomic weight of antimony should be redetermined.

The product obtained by roasting antimony trisulphide is said to contain antimony tetroxide. In presence of this oxide, low values are obtained when the sulphide is estimated by the method

described above, and this is attributed to the oxidation of the hydrogen sulphide by the antimony tetroxide. Satisfactory results may be obtained if the substance is boiled with 25% potassium hydroxide, and the solution reduced by the addition of metallic aluminium when the antimony is precipitated. The hydrogen sulphide is then liberated by the addition of acid and absorbed in 3—4% sodium hydroxide solution.

According to Rose, the tetroxide may be estimated by heating with excess of antimony trisulphide in an inert atmosphere, when sulphur dioxide is set free according to the equation $Sb_2S_3 + 9Sb_2O_4 = 10Sb_2O_3 + 3SO_2$. Experiments made by the author with mixtures of the trisulphide and the tetroxide which were heated in a current of carbon dioxide gave much larger quantities of sulphur dioxide than correspond with this equation. Further investigation has shown that the carbon dioxide is acted on by antimony trisulphide at a dull red heat with the formation of sulphur dioxide, carbon monoxide, and carbon oxysulphide. This reaction precludes the possibility of estimating the higher oxides of antimony by fusion with the trisulphide in an atmosphere of carbon dioxide. Since it has also been found that sulphur dioxide is formed by the interaction of the trioxide with the trisulphide in an inert atmosphere, it follows that the liberation of sulphur dioxide cannot even be used as a qualitative test for the presence of higher oxides in the products obtained in the roasting process. H. M. D.

Microscopical Methods, with Special Reference to the Examination of Drugs. Henry G. Greenish (*Analyst*, 1916, **41**, 195—201).—Methods are described for the identification and determination of the purity of simple powders, for the estimation of the composition of a compound powder, and for detecting drug powders under certain unusual conditions, for example, in fæces. For the identification of a drug, a microscopical examination of sections of the larger particles, followed by an examination of specimens of the fine powder mounted in water, dilute glycerol, and chloral hydrate solution, is recommended. Recourse must be had to identification tables, and in every case identification should be confirmed by comparison with a genuine powder. The microscopical examination of a powdered drug will afford evidence as to whether the powder has been prepared from a drug which has been attacked by the larvæ of various beetles; such a drug is obviously of inferior quality. The method of detecting remains of beetles depends on the highly resistant nature of the chitinous portions of the insect, and consists in treating the powder successively with ether, boiling dilute hydrochloric acid, water, concentrated sulphuric acid, and chromic acid solution; the residual matter after this treatment will consist chiefly of sand and beetle. Systematic search of the powder and possible identification of the constituents is the only way of determining the composition of a compound powder. Stress is laid on the importance of making sketches of the structures, etc., observed. To prepare fæces for microscopical examination, the substance should be mixed with water, shaken with ether, then with ether

and alcohol, mixed with water, and strained through muslin. The larger fragments on the muslin are washed and examined in glycerol or chloral hydrate solution; the strained liquid is submitted to centrifugal action, and the sediment examined directly and also after treatment with chloral hydrate. The original should be consulted for the full details of the methods described. W. P. S.

Quantitative Micro-elementary Analysis of Organic Substances. I. J. RINKES (*Chem. Weekblad*, 1916, **13**, 800–803).—The author has obtained satisfactory results in the application of Dubsky's method of micro-analysis to the estimation of carbon, hydrogen, and nitrogen in organic compounds. A. J. W.

Detection of Methyl Alcohol by Denigès' Method. E. SALKOWSKI (*Zeitsch. Nahr. Genussm.*, 1914, **28**, 225—236).—A critical examination of Denigès's method (A., 1910, ii, 461) in combination with modifications described by Fincke (A., 1913, ii, 947; 1914, ii, 303) showed that many different alcoholic liquids yield a distillate which gives a reaction indicating the presence of methyl alcohol. Even when the distillate has been re-distilled before being tested, the result is not conclusive. A feeble reaction may be due to the presence of glycerol, but a strong reaction may be taken as indicating the presence of methyl alcohol; confirmatory tests should be applied in every case where the presence of methyl alcohol is suspected or indicated by the above-mentioned tests. W. P. S.

New Colour Reaction for "Oxycholesterol." MARY CHRISTINE ROSENHEIM (*Biochem. J.*, 1916, **10**, 176—182).—On adding a few drops of commercial methyl sulphate to a solution of cholesterol in chloroform, the solution remains colourless for some minutes; but on slightly warming in a water-bath it gradually assumes a bright raspberry-red colour showing a blue fluorescence in sunlight. Spectroscopic examination reveals two absorption bands, one between *D* and *E*, and the other near *F*. On adding a drop of 5% ferric chloride solution in glacial acetic acid, the colour changes to a deep purple, showing an absorption band in the blue part of the spectrum.

When a solution of "oxycholesterol" in chloroform is similarly treated with a few drops of commercial methyl sulphate, an immediate purple colour is produced without warming. The solution on spectroscopic examination shows an absorption band in the yellow part of the spectrum. On adding a drop of the ferric chloride solution, the colour changes first to greenish-blue and then to emerald-green with a green fluorescence. The green colour is discharged by water, acetone, or alcohol, but not by glacial acetic acid. When examined spectroscopically, it shows a characteristic absorption band in the red.

The first part of each of the above tests is not given when pure methyl sulphate is employed, but if the pure methyl sulphate is heated to the boiling point and then cooled it behaves like the

commercial material. The essential constituent is probably methyl hydrogen sulphate. Both the pure and the commercial methyl sulphates give the typical reactions after the treatment with the ferric chloride solution.

Phytosterols and oxyphytosterols behave exactly like the cholesterol compounds when tested by the above reagents. H. W. B.

Marcusson-Schilling's Modification of Bömer's Method for the Detection of Phytosterol, by Precipitation with Digitonin. A. Olig (*Zeitsch. Nahr. Genussm.*, 1914, **28**, 129—138. Compare A., 1913, ii, 885).—Results of analyses of numerous mixtures of animal and vegetable fats showed that the melting point of the acetate, after the first or second crystallisation, almost always indicated whether phytosteryl acetate was present with the cholesteryl acetate. The presence of paraffin and of certain waxy or resinous constituents of shea and mowrah fats did not interfere with the test. In most cases it is sufficient to precipitate the cholesterol and phytosterol with digitonin directly from the fat; previous saponification of the fat and precipitation with digitonin from the fatty acids is necessary only when the direct precipitation from the fat yields an inconclusive result, but this seldom occurs in practice.
W. P. S.

Detection of Phytosterol in Animal Fats by Precipitation with Digitonin. B. Kuhn and J. Wewerinke (*Zeitsch. Nahr. Genussm.*, 1914, **28**, 369—379. Compare A., 1915, ii, 844).—Precipitation of the cholesterol and phytosterol by digitonin is more trustworthy than Bömer's original method for the detection of phytosterol in animal fats. The precipitation should be made from the fatty acids, and not directly from the fats (compare A., 1914, ii, 586). W. P. S.

Estimation of Phytosterol in Vegetable Fats. Max Klostermann and Herm. Opitz (*Zeitsch. Nahr. Genussm.*, 1914, **28**, 138—145).—The quantity of phytosterol in vegetable oils varies from 0·133% in the case of olive oil to 0·549% in sesame oil; in many of the vegetable oils a large proportion of the phytosterol is present in the form of its ester. In the detection of vegetable oils in animal fats it is therefore advisable to saponify the fat before the phytosterol and cholesterol are precipitated with digitonin, since the latter precipitates the free alcohols only. It is pointed out that the quantity of phytosterol in a vegetable oil depends on the method by which the oil has been obtained from the seeds, &c. W. P. S.

Estimation of Blood Sugar. Hugh MacLean (*J. Physiol.*, 1916, **50**, 168—181).—See this vol., i, 613.

The Enzymes of Honey. F. Gothe (*Zeitsch. Nahr. Genussm.*, 1914, **28**, 273—286).—Honey does not contain lactase, proteases, or

lipases, and the presence of inulase is doubtful. Invertase is present, a larger quantity being found in natural honey than in honey from bees which have been fed with sugar. The invertase has a maximum activity at 40°, and is destroyed by heating at 60° for one hour. Catalase and diastase are present; the diastase content frequently increases as the catalase diminishes. The activity of a solution of these two enzymes is considerably decreased when the solution is filtered. A dirty or impure honey has a very high catalase number; a low catalase number does not indicate that the honey is inferior in quality or that it has been heated. The activity of the catalase is seriously affected, however, when the honey solution is heated at 60° for one hour, but the honey itself may be heated at 70° before the effect of temperature is observed.

W. P. S.

Properties of Honey Diastase. F. GOTHE (*Zeitsch. Nahr. Genussm.*, 1914, **28**, 286—321).—The author points out that the estimation of the activity of the diastase in honey affords a means of ascertaining whether any given sample of honey is natural honey. A high diastase number (Wohlgemuth's method, A., 1908, ii, 444) indicates pure honey; if the diastase number is low, Fiehe's test and the precipitin reaction will afford confirmatory evidence of the presence of adulterants. The opinion is expressed that a honey which has no enzymic activity should not be called natural honey. The activity of the diastase is destroyed when the honey is heated at 70°; a honey so treated loses its aroma and biological properties, and is considered to be a denatured product. In the estimation of the diastatic power of a honey the prescribed conditions should be observed; the starch solution employed should be freshly prepared. The presence of acids or alkalies in any considerable quantity interferes with the activity of the enzyme; prolonged contact with alcohol, filtration, and dialysis have the same effect.

W. P. S.

Colorimetric Method for the Detection of Potato Starch. GUSTAV BLUNCK (*Zeitsch. Nahr. Genussm.*, 1915, **29**, 246—247).—The dye called "metachrome-red G Agfa" colours potato starch and cell tissues a bright golden-yellow, but it does not colour cereal starches. The presence of potato starch in ordinary flour may be detected by treating a portion of the latter on a microscope slide with a drop of water, drying it, adding a drop of the dye solution, washing off the excess of the latter, and then examining the slide under the microscope. The dye solution is prepared by saturating boiling 30% alcohol with the substance, filtering the cooled solution, and diluting it with 25% of its volume of water. In applying the test to bread, it is necessary to treat a small quantity of the crumb with dilute alkali solution, and then wash it thoroughly before the dye is added. This treatment removes the acidity of the bread, which is essential, since in the presence of acids the dye colours wheat starch as well as potato starch.

W. P. S.

Estimation of Ferro- and Ferri-cyanides in the Presence of Cyanides and Thiocyanates. FREDK. G. W. KNAPMAN and ERNEST L. RANDALL (*Chem. News*, 1916, **113**, 265—266).—The volumetric method described depends on the reduction of ferricyanides by titanium trichloride. *Estimation of ferricyanide alone.*—The solution, containing about 0·1 gram of the salt in 50 c.c. of water, is treated with 2 grams of ammonium thiocyanate and titrated with standardised titanium trichloride solution; at first the green colour of the solution deepens, then becomes paler, and finally changes abruptly to a golden-brown precipitate. *Ferrocyanide alone.*—The solution is rendered slightly acid with sulphuric acid, dilute potassium permanganate solution is added until a yellowish-red colour is produced, an excess of ammonium thiocyanate is then added, and the ferricyanide (resulting from the oxidation of the ferrocyanide) is titrated as described. If thiocyanate is present with the ferrocyanide, the latter must be oxidised by heating the solution for twenty minutes at 60° with an excess of iodine solution; the excess of iodine is then titrated with thiosulphate solution, ammonium thiocyanate is added, and the mixture titrated with titanium trichloride solution. *Mixture of ferricyanide, ferrocyanide, thiocyanate, and cyanide.*—A portion of the solution is titrated with sulphuric acid, using phenolphthalein as indicator (this operation removes the alkalinity due to the cyanide), ammonium thiocyanate is then added, and the ferricyanide titrated. Another portion of the solution is titrated with sulphuric acid, the ferrocyanide is oxidised with iodine as described above, and the total ferricyanide then estimated. W. P. S.

Electrolysis of Alkaline Solutions of Potassium Thiocyanate. W. J. CROOK, L. E. BOOTH, and A. THIEL (*J. Soc. Chem. Ind.*, 1916, **35**, 688; from *Met. and Chem. Eng.*, 1916, **14**, 587—591). —Dilute solutions of potassium thiocyanate of known strength, with and without potassium hydroxide, were electrolysed for five hours by currents of 0·5—4·0 amperes at 2·7—8·9 volts, and examined hourly. In alkaline solutions, the only products were potassium cyanide and sulphate, formed probably according to the equation $KCNS + 3O + 2KOH = KCN + K_2SO_4 + H_2O$. In neutral solutions hydrogen cyanide was evolved, and the solution became acid. Methods are given for the estimation of potassium thiocyanate and its possible decomposition products (cyanide, sulphate, hydroxide, cyanate, carbonate, and sulphite) in presence of each other. G. F. M.

Apparatus for the Estimation of Urea in Cerebrospinal Fluid. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1915, **96**, 335—341).—The apparatus described and figured in the text is a modification of the manometric apparatus for the estimation of urea devised by Löb and Prorok (A., 1914, ii, 687). The instrument is smaller and the "dead space" is reduced to a minimum. It is thus

adapted for the estimation of the comparatively minute quantities of urea present in the cerebrospinal fluid. The method of manipulation is similar to that required in the case of the original apparatus. H. W. B.

The Ureolytic Action of Soja Beans. D. H. WESTER (*Chem. Weekblad*, 1916, **13**, 663—677; *Pharm. Zentr.-h.*, 1916, **57**, 423—430).—An investigation of the influence of age, antiseptics, sunlight, and temperature on the activity of soja beans. The author has obtained very good results with these products in the estimation of urea in urine, and confirms Marshall's observation (A., 1913, ii, 640, 991) that the presence of dextrose even in considerable proportion does not detract from the accuracy of the method. A. J. W.

A New Colour Reaction for Alkaloids and Similar Substances. JUAN PESET and ROGELIO BUENDÍA (*Anal. Fis. Quim.*, 1916, **14**, 257—263).—Many alkaloids and allied products give characteristic colorations with sulphuric acid containing a small proportion of titanic acid. A. J. W.

Fluorescence of Alkaloids and its Application in Toxicological Investigations. ROBERT HELLER (*Intern. Zeitsch. phys. chem. Biol.*, 1916, **2**, 397—411).—The alkaloids and their compounds exhibit characteristic fluorescent phenomena when excited by ultraviolet light. The luminescence-microscope devised by Lehmann (*Zeitsch. wiss. Mikroscopie*, 1913, **30**, 449) is employed, and the various alkaloids of toxicological importance are classified in groups according to the colour and intensity of the observed fluorescence. The formation of derivatives, such as salts, of the alkaloids is accompanied by an alteration in the colour and intensity of the fluorescence, which varies greatly in extent in the case of each alkaloid. The identity of an alkaloid is therefore more readily established when the fluorescent properties of its salts are also ascertained. For the purpose of examination, the alkaloid must be pure and in the form of a fine powder; a trace of impurity materially alters the character of the fluorescence. H. W. B.

Microchemical Toxicology. O. TUNMANN (*Chem. Zentr.*, 1916, i, 313—314; from *Apoth. Zeit.*, 1915, **30**, 678—679, 686—688).—A description is given of the application of microchemical methods to toxicological analysis. For the detection of alkaloids, sublimation and recrystallisation of amorphous precipitates, as well as the precipitation of crystalline compounds, have advantages over colour reactions; the latter, however, may be carried out on microscope slides. If a drop of aconitine solution is treated with Mecke's reagent, a violet coloration appears within a few minutes at the edge of the drop; after some hours the colour changes to brick-red. When crystallised from toluene, aconitine forms flat

plates, which soon collect in nodular clusters; rhombic crystals form from a solution of the alkaloid in amyl alcohol, the same crystals separating from a benzene solution, but in this case numerous prismatic crystals are also produced. Yellow crystals are obtained on treating a drop of aconitine solution with iodine solution, dissolving the precipitate in alcohol, and allowing the mixture to evaporate slowly under a cover-glass. Similar crystals are produced by the action of hydriodic acid on the alkaloid.

W. P. S.

Estimation of Creatine in Muscle. III. LOUIS BAUMANN and THORSTEN INGVALDSEN (*J. Biol. Chem.*, 1916, **25**, 195—200. Compare this vol., ii, 358).—The creatine in the muscle extract is converted into creatinine, which is then quantitatively precipitated as the potassium picrate salt by the addition of excess of picric acid and potassium picrate. The salt is then decomposed with sulphuric acid, and the liberated creatinine estimated colorimetrically with picric acid and sodium hydroxide in the usual way. The values obtained agree closely with those found by the direct methods of Baumann and others (*loc. cit.*). H. W. B.

Methyl-red as an Indicator in the Estimation of Nicotine by Toth's Method. PAUL SCHICK and GÉZA HATOS (*Zeitsch. Nahr. Genussm.*, 1914, **28**, 269—270).—Methyl-red may be used in place of iodoeosin as the indicator in the titration of nicotine in the ethereal solution of the alkaloid obtained according to Toth's method (A., 1901, ii, 363, 708). W. P. S.

Estimation of Alizarin in Dyed Cotton Fabrics, and an Attempt to Ascertain the Composition of Turkey-red and other Alizarin Lakes. W. N. LEIGH (*J. Soc. Dyers*, 1916, **32**, 205—213).—Knecht and Hibbert (this vol., ii, 120) suggested that their method for the estimation of alizarin might be applied to the dyed fabric, and therefore prove useful in examining the composition of alizarin lakes. The present paper deals with these problems.

For the estimation of alizarin on the fibre the following procedure is recommended. From 1·5 to 3 grams of the dyed cotton are dissolved in 10 c.c. of 80% sulphuric acid at a temperature not above 40°. The bright red, viscous solution is then diluted to about 100 c.c., and the precipitated alizarin is filtered, extracted with alcohol, and titrated by Knecht and Hibbert's method. The small amount of dye which remains in solution is titrated by boiling the filtrate with excess of titanous chloride in an atmosphere of carbon dioxide and determining the excess by a back titration with ferric alum in the presence of potassium thiocyanate. Since arsenic compounds are reduced by titanous salts, the method is not trustworthy in the case of fabrics which have been fixed by arsenates.

Details are given of the analyses of various samples of Turkey-red as it actually exists on the fibre, and also of a chromium and an iron lake. It is shown that the proportions of alizarin to alumina and lime vary greatly, and are seldom represented by simple mole-

cular proportions. The suggestion is made that the Turkey-red lake is dissolved in an excess of the aluminium salts of the fatty acids which are met with in the oil which is applied to the fibre. This fatty matter is so firmly fixed to the fibre that solvents do not affect it, and it is even difficult to remove it from the isolated lake.

J. C. W.

Detection of Albumin in Urine. LIEBERS (*Chem. Zentr.*, 1916, i, 773—774; from *Deutsch. Med. Woch.*, 1916, **42**, 323).—Pandy's reaction for the detection of protein in cerebrospinal fluid can be adapted for the examination of urine. A watch-glass is filled three-parts full with a dilute phenol solution (liquefied carbolic acid, 10%), and when the solution has completely cleared 1—2 drops of urine are added. In presence of albumin, a white cloudiness or precipitate is immediately formed, according to the amount present. The test is as sensitive as the acetic acid–ferrocyanide reaction.

G. F. M.

New Process to Remove the Humic Substances Formed by the Acid Hydrolysis of Organic Substances. A. CLEMENTI (*Chem. Zentr.*, 1916, i, 721—722; from *Arch. Farm. sperim.*, 1915, **20**, 561—566).—The coloured humic substances which disturb the formol titration of hydrolytic products, can be removed by the addition of colloidal ferric hydroxide in presence of an electrolyte. The resulting clear solutions give the same amino-acid values as when decolorisation is carried out by other methods, such as barium sulphate precipitation.

G. F. M.

Chemical and Physical Analysis of Blood. A. O. GETTLER and WILLIS BAKER (*J. Biol. Chem.*, 1916, **25**, 210—222).—See this vol., i, 576.

Analysis of Rhamnus Barks. O. TUNMANN (*Chem. Zentr.*, 1916, i, 314; from *Apoth. Zeit.*, 1915, **30**, 642).—The red-coloured foam which is obtained when drugs containing anthraquinones are shaken with sodium hydroxide solution (compare this vol., ii, 404) is probably due to the presence of chrysophanol; the latter is present, therefore, in *Rhamnus carniolicus* as well as in *R. catharticus*, and the reaction simply serves to distinguish these from the American rhamnus bark, *R. purshiana*. Tschirch's colorimetric method shows that the quantities of anthraquinone derivatives in *R. frangulus* and in *R. purshiana* have a ratio of 4:1, whilst according to the author's gravimetric method (this vol., ii, 60) the ratio between the two respective quantities is 3 or 2·5:1. Physiological experiments would probably indicate whether this difference exists or whether any value is to be ascribed to other substances accompanying the quinols in the barks.

W. P. S.

General and Physical Chemistry.

Atomic Refraction. ADOLF HEYDWEILLER (*Ber. Deut. physical Ges.*, 1914, **16**, 722—727).—A summary is given of the values which have been deduced in previous papers (compare A., 1915, ii, 645, 919) for the refractive powers of different atoms from measurements of the refractive index of salt solutions. The atomic refractivities have been reduced to values corresponding with long waves, and since the observations refer exclusively to electrically charged atoms in the free condition, these values are not affected by those disturbing factors which necessarily influence the atomic refractivities deduced from the molecular refractivities of compounds.

When the values are plotted against the atomic weight, a series of similar curves is obtained, showing clearly that the atomic refraction is a periodic function of the atomic weight. H. M. D.

Facts and Conclusions in Relation to the Number and the Coupling of Electrons in the Hydrogen Atom. J. STARK (*Ann. Physik*, 1916, [iv], **50**, 53—88).—A detailed discussion of the bearing of recent observations on the spectral emission of hydrogen on the question of the constitution of the hydrogen atom.

H. M. D.

The Ultra-red Spectra of Gases. III. The Configuration of the Carbon Dioxide Molecule and the Laws of Intramolecular Forces. NIELS BJERRUM (*Ber. Deut. physical Ges.*, 1914, **16**, 737—753).—Recent observations have furnished support for the view that the ultra-red spectrum is to be attributed to vibrational or rotational movements of atoms or atomic groups. This view is submitted to a more detailed analysis by reference to the ultra-red spectrum of carbon dioxide. The fact that this shows three bands at $\lambda = 2{\cdot}7$, $4{\cdot}3$, and $14{\cdot}7\,\mu$ indicates that the molecule possesses three degrees of freedom, and by making certain assumptions as to the nature of the forces acting between the atoms in the molecule which result in the setting up of vibrations corresponding with these bands, it is shown that certain conclusions may be drawn relative to the configuration of the carbon dioxide molecule. The influence of molecular rotation on the bands emitted by the vibrating atoms is also considered, but the experimental observations relative to the constitution of the three bands cannot be reconciled with the possible configurations which are suggested by the wavelengths of the bands. It is shown, however, that the calculated amplitudes of the vibrations are not at all inconsistent with the molecular structures which are suggested by the above analysis.

H. M. D.

The Optical Behaviour of Water of Crystallisation. CLEMENS SCHAEFER and MARTHA SCHUBERT (*Ann. Physik*, 1916, [iv], **50**, 339—345).—Water in the free condition shows an ultra-red absorp-

tion band at 3·2 μ, but according to observations on crystalline salt hydrates, the frequency of vibration of combined water corresponds with a greater wave-length. The displaced maximum in the case of hydrated copper sulphate lies, for instance, at about 3·5 μ.

In the further investigation of this effect, experiments were made with the alums, and it has been found that these isotropic crystals give a reflexion curve which shows two maxima corresponding with the wave-lengths 3·5 and 3·05 μ. According to Werner, molecules containing twelve molecules of water of crystallisation are supposed to contain water in an associated form, so that an alum would be represented by the formula $(M'6H_4O_2)M'''(SO_4)_2$, and it is suggested that the occurrence of two maxima may be due to this.

Attention is drawn to the fact that the absorption maximum of water at $\lambda = 3{\cdot}2\ \mu$ is also displaced when salts like calcium chloride are added, and this is supposed to be connected with the formation of hydrated molecules or ions.

Observations on uniaxial crystals of nickel sulphate, which were made with polarised rays, show that there is a simple displacement of the maximum when the plane of polarisation is perpendicular to the optical axis, but that a double maximum appears when the plane of polarisation is parallel to the optical axis. The combined water is therefore dichroitic. Similarly, observations made with potassium magnesium sulphate, potassium zinc sulphate, and ammonium zinc sulphate, which form biaxial crystals, show that the combined water is trichroitic.

The observations indicate that the water of crystallisation in optically anisotropic crystals is itself anisotropic, and behaves optically in accordance with the symmetry relations of the crystal.

H. M. D.

Short-waved Ultra-red Characteristic Frequencies of the Sulphates and Carbonates. CLEMENS SCHAEFER and MARTHA SCHUBERT (*Ann. Physik*, 1916, [iv], **50**, 283—338).—The characteristic ultra-red vibration frequencies up to $\lambda = 20\ \mu$ have been determined for thirty-four sulphates and fifteen carbonates by a reflexion method. Observations were made with ordinary and polarised light.

The reflexion curves for the sulphates show two well-developed maxima at about 9 μ and 16 μ. In the case of the isotropic sulphates (alums), the maximum at 9 μ appears to correspond with a single frequency, although the employment of greater dispersion may disclose complex structure. For uniaxial crystals the maxima at both 9 μ and 16 μ show the existence of two characteristic frequencies, corresponding with the ordinary and extraordinary rays respectively. In the case of biaxial crystals the maximum at 9 μ consists of three separate vibrations corresponding with the three refractive indices. It is probable that the structure of the maximum at 16 μ is of the same type. The two selective frequencies which are shown by all the sulphates examined are obviously connected with the SO_4 group.

The curves of reflexion for the carbonates exhibit maxima at

about 6·5, 11·5, and 14·5 μ, and these are presumably due to the CO_3 group. For negative uniaxial crystals, the maxima at 6·5 and 14·5 μ correspond with the ordinary ray and the maximum at 11·5 μ with the extraordinary ray. In the case of negative biaxial crystals the maxima at 6·5 and 14·5 μ consist of two characteristic vibrations corresponding with the axes of greatest and mean refractive index, whilst the maximum at 11·5 μ belongs to the axis of smallest refractive index.

From a comparison of the data obtained it appears that the anisotropy of the characteristic frequencies in the maxima of reflexion is the more pronounced the greater the difference between the refractive indices for rays in the visible region of the spectrum. Since the dispersion and double refraction in the visible region is determined by the ultra-violet characteristic frequencies, it follows that there is some connexion between characteristic vibrations in the ultra-violet and ultra-red regions.

The observations with hydrated salts indicate that the characteristic frequency of water at $\lambda = 3·2\ \mu$ is displaced as a result of chemical combination. H. M. D.

The Absorption of Ultra-violet Rays by the Bromo-derivatives of Methane. GUSTAVE MASSOL and A. FAUCON (*Compt. rend.*, 1916, **163**, 92—94. Compare A., 1914, ii, 695).—An examination of the absorption spectra of di-, tri-, and tetra-bromomethane. The results show that the characteristic absorption band of bromine in solution, $\lambda = 295 - 248$, is not given by any of the bromo-derivatives of methane. The smaller the number of bromine atoms in the molecule, the more transparent are the compounds to ultra-violet rays. Each bromo-derivative is less transparent than the corresponding chloro-derivative, examined under the same conditions of concentration and thickness. W. G.

The Fluorescence of Iodine Vapour. I. WILHELM H. WESTPHAL (*Ber. Deut. physikal. Ges.*, 1914, **16**, 829—834).—Experiments made with iodine vapour of constant density have shown that the intensity of the fluorescence under the influence of a constant source of excitation diminishes as the temperature rises. By comparison with observations of Wood and Spens (A., 1914, ii, 233), who examined the dependence of the fluorescence on the density of the vapour, it appears that the intensity is not only affected by the frequency of collision between the iodine molecules, but also by the average distance of separation of the molecules.
H. M. D.

Decay of the Activity Induced in Chlorine by the Action of Light and the Combination of Chlorine and Hydrogen. M. VOLMER (*Zeitsch. Elektrochem.*, 1916, **22**, 255—256).—Polemical against Bodenstein (this vol., ii, 463), and an answer to criticisms of the author's work (A., 1915, ii, 205). J. F. S.

Velocity of Photochemical Reduction of Aliphatic-Aromatic Ketones. W. D. COHEN (*Chem. Weekblad*, 1916, **13**, 902—906).—Experiments to determine the velocity of reduction by photo-

chemical methods of ketones have proved that the presence of aliphatic groups exercises a retarding or inhibiting influence on the process. Benzophenone is readily reduced, phenyl benzyl ketone and acetophenone slowly, but dibenzyl ketone and acetone undergo practically no reduction. A. J. W.

Temperature-coefficients of Phototropic Transformations in Monochromatic Light. II. M. PADOA and A. ZAZZARONI (*Atti R. Accad. Lincei*, 1916, [v], **25**, i, 808—811. Compare A., 1915, ii, 678).—The temperature-coefficient for the coloration of benzaldehydephenylhydrazone has the values 1·08 and 1·04 for blue and violet lights respectively, the value obtained by Padoa and Minganti for white light (A., 1914, ii, 191) being 1·066. Thus, the value of the temperature-coefficient increases with the wave-length of the light. The results obtained with benzil *o*-tolylosazone for white and blue lights are also in agreement with this rule.

With triphenylfulgide, the velocity-coefficients are: (1) coloration, 1·29 and 1·67 in blue and green lights respectively; (2) decolorisation, 0·89 and 1·08 in yellow and red lights respectively. An instance of a reaction with a temperature-coefficient less than 1 has been observed previously by Skrabal and Weberitsch (A., 1914, ii, 187). In the present case the velocity of the reaction should be independent of the temperature for light of a certain wave-length.

T. H. P.

The Selective and Normal Photoelectricity of Potassium. G. WIEDMANN (*Ber. Deut. physikal. Ges.*, 1915, **17**, 343—349).—Previous experiments by Wiedmann and Hallwachs (A., 1914, ii, 162) showed that the photoelectric sensitiveness of potassium is greatly reduced when the metal is subjected to repeated distillation in the highest possible vacuum. This observation, although confirmed by Fredenhagen (A., 1914, ii, 327), is contradicted by results obtained by Pohl and Pringsheim (A., 1914, ii, 405), who found no change in the magnitude of the selective photo-electric effect after prolonged boiling and repeated distillation of the metal in a vacuum.

New experiments by the author have given results in substantial agreement with the previous measurements, the photoelectric sensitiveness falling to 1% of its original value when the contained gases were removed as completely as possible by distillation of the metal. In regard to the region of selective action, the new experiments show that the selective action disappears when the traces of foreign gases are eliminated. The selective effect reappears if a feeble discharge is passed through the cell with the potassium serving as cathode. H. M. D.

Photoelectric Discharge from Leaves. J. A. McCLELLAND and R. FITZGERALD (*Proc. Roy. Irish Acad.*, 1916, **33**, *A*, 1—8).—The photoelectric discharge from leaves and flowers subjected to the ultra-violet rays emitted by a spark between aluminium electrodes has been compared with the discharge from a freshly cleaned

copper plate. Green leaves gave an effect varying from 3% to 10% of that of copper, whilst flowers of various colours gave smaller effects, usually less than 1% of the copper effect.

Acetone extracts of chlorophyll were found to be inactive, but when the chlorophyll is precipitated by dilution with large quantities of water, it shows photoelectric activity, which decays rapidly, however, under the action of the exciting radiation.

Comparatively large effects, reaching up to 50% of that of copper, are shown by solutions which are obtained by immersing leaves in distilled water. The activity of these solutions is greatly increased by the action of oxidising agents such as lead dioxide and potassium permanganate. A similar increase in the photoelectric activity is observed when these oxidising agents are added to aqueous solutions of various organic substances. Closed-ring compounds show this effect more markedly than open-chain compounds.

The observations support the view that the emission of electrons is facilitated by chemical change. H. M. D.

The Röntgen Spectra of the Elements Sodium to Chromium. MANNE SIEGBAHN and WILHELM STENSTRÖM (*Physikal. Zeitsch.*, 1916, **17**, 318—319).—Wave-length measurements have been made in the high-frequency spectra of the elements with atomic numbers ranging from 11 to 26. As the atomic weight falls, the intensity of the β_1 and β_2 lines diminishes. The spectra of the lighter elements exhibit two new lines, α_3 and α_4, which lie close to α_1 and α_2, but are of somewhat shorter wave-length. H. M. D.

The Absorption Band K of the Elements for X-Rays, followed from Bromine to Bismuth, and the Emission of a Coolidge Tube towards the Very Short Wave-lengths. M. DE BROGLIE (*Compt. rend.*, 1916, **163**, 87—90).—Further measurements of the coefficient of absorption by a given simple substance of a series of *X*-rays in the form of the fluorescence rays of a series of simple substances arranged in the order of increasing atomic weights, shows that it is possible, using tungsten as the anticathode, to follow the absorption band of an element at least as far as bismuth. The value for bismuth corresponds with a wave-length of $1{\cdot}3 \times 10^{-9}$ cm., that of thorium being still lower. The position of the bands appears to be independent of the physical or chemical state of the elements which they characterise, and on their observation a rapid and convenient method of spectrum analysis can be framed, requiring only a few decigrams of the substance. The *K* group for tungsten comprises a doublet, $2°06' - 2°04'$, and another at about $1°50'$. Immediately after, as regards short wave-lengths, an intense emission band commences, which is continued as far as the most penetrating rays emitted by the tube. This fact, taken in conjunction with the other results, puts out of doubt the presence in the radiation of a tube of rays much more penetrating than the *K* rays of its anticathode.

W. G.

Revision of the Atomic Weight of Thorium. Analysis of Thorium Bromide. OTTO HÖNIGSCHMID and STEFANIE HOROVITZ (*Monatsh.*, 1916, **37**, 305—334).—The international value of the atomic weight of thorium, 232·4, depends on the conversion of anhydrous thorium sulphate into oxide, and this method is adversely criticised. By means of the quartz apparatus, previously used for the atomic weight of uranium, the preparation of thorium bromide, by the action of bromine on a mixture of thorium oxide and carbon, and its sublimation and transference into the weighing tube has been successfully accomplished. The operation is difficult, the thorium bromide is volatile without decomposition only within somewhat narrow limits of temperature, and for each analysis a separate preparation of the bromide has to be made. A temperature of about 1000° is needed in the preparation.

The thorium employed was (1) from repeated recrystallisations of a very large quantity of thorium ammonium nitrate, provided by the Auergesellschaft, (2) a preparation provided by R. I. Meyer which had been purified by the sulphate method, followed by the iodate method, and passed through the bromide preparation once before use. Both gave identical results.

The atomic weight estimations followed the well-known methods of T. W. Richards. In two independent series of twelve and fifteen analyses respectively, the values $232·15 \pm 0·016$ and $232·12 \pm 0·014$ were obtained, and the latter value, 232·12, is regarded as the more probable. Incidentally, Baxter's value of 79·916 for bromine, when silver is 107·880, was exactly confirmed.

F. S.

Concerning the Atomic Weight of Ionium. OTTO HÖNIGSCHMID and STEFANIE HOROVITZ (*Monatsh.*, 1916, **37**, 335—345. Compare preceding abstract).—The atomic weight of ionium, according to the disintegration theory, should be either $238·18 - 8 = 230·18$, if calculated from that of uranium, or $226·0 + 4 = 230·0$ if calculated from that of radium. The minute quantity of thorium in Joachimsthal pitchblende and the very high α-activity of the thorium separated, which is due to the isotope ionium, indicates that its atomic weight ought to be appreciably lower than that of ordinary thorium. The bromide method, described in the preceding abstract, is sufficiently accurate to test this.

The ionium preparation was that separated by Auer von Welsbach and examined spectroscopically by Exner and Haschek. It was twice precipitated as iodate, and further purified by Brauner's oxalate method. When examined spectroscopically by Haschek and compared with the purified material on which the atomic weight of thorium had been determined, both showed identical spectra, completely free from those of other rare earths and of cerium.

The atomic weight of the ionium preparation in three determinations, by the same method as that employed for thorium, gave $231·51 \pm 0·014$, which is 0·6 unit lower than that found for thorium prepared from monazite. Assuming 230·0 as the true atomic weight of ionium, there is 30% ionium and 70% of thorium in the

preparation. This furnishes a further example of two materials chemically and spectroscopically identical differing in atomic weight. F. S.

The Life-period of Ionium and some Consequences that follow its Determination. STEFAN MEYER (*Monatsh.*, 1916, **37**, 347—355).—The atomic weight determination of the ionium preparation of Auer von Welsbach (preceding abstract) and its α-activity give the period of average life of ionium. From the range of the α-rays this has been estimated indirectly as 200,000, 330,000, and 74,000 years. From the rate of growth of radium from uranium over ten years a minimum period of average life of 100,000 years, which cannot be far from the actual period, has been assigned (Soddy and Hitchins). A maximum period of three times (Meyer and Hess) and 5·6 times this (Boltwood) has been obtained from the intensity of α-radiation, by assuming the ionium–thorium preparations separated from pitchblende to be pure ionium. The first refers to the Welsbach preparation which the atomic weight shows to contain about 30% of ionium, or 29·5% as a mean estimate, to 70·5% of thorium. The α-rays from a drop of this preparation spread over a large surface gave an ionisation corresponding with 5·84 *E.S.U.* per mg. of thorium–ionium. A comparison of this with that given by radium in similar circumstances shows that the periods are as 1 : 0·0172, and therefore, assuming for radium 2500 years, the period of average life of ionium is $1·45 \times 10^5$ years (period of half change almost exactly 10^5 years). The value of the range of the α-particles calculated from this period is 2·914 cm. at *N.T.P.*, which differs from the experimental value, 2·95 cm., within the error of the experiment.

The following consequences are deduced: (1) per 1 gram of radium in pitchblende there are 58 grams of ionium, along with 139 grams of thorium, a total of thorium isotopes of 197 grams; (2) the international radium standard contained when prepared $5·6 \times 10^{-8}$ grams of mesothorium per gram, which can affect its α- and γ-activity by two or three thousandths per cent., which is far below the limit of exactitude of radioactive measurements. F. S.

The Absorption of Gases in Vacuum Tubes. S. BRODETSKY and B. HODGSON (*Phil. Mag.*, 1916, [vi], **32**, 239. Compare this vol., ii, 285).—A note admitting the priority of Vegard (*Videnskapselskapets Skrifter*, 1913, No. 7, Christiania) in respect of certain observations made by the authors. H. M. D.

The Electric Absorption of Gases in Vacuum Tubes. L. VEGARD (*Phil. Mag.*, 1916, [vi], **32**, 239—242).—Attention is called to earlier results obtained by the author (compare preceding abstract) which agree closely with those obtained more recently by Brodetsky and Hodgson. With reference to the theoretical deduction of the absorption curve, it is pointed out that the assumptions made by these investigators involve a continuous increase in the rate of absorption with increase in the cathode fall when the current is

kept constant, whereas all the experimental evidence shows that there is an upper limit for the velocity of absorption. H. M. D.

The Specific Conductivity of Pure Water in Equilibrium with Atmospheric Carbon Dioxide. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1916, **38**, 1480—1497).—The fact that carefully purified water in contact with air has a very nearly constant conductivity equal to $0.7-0.8\times10^{-6}$ mho, has led to the view that the conducting impurities consist almost entirely of carbonic acid derived from the atmosphere. To test this explanation the author has calculated from available and new data the conductivity of a solution of carbonic acid in equilibrium with the atmosphere, and finds that the calculated values 0.65×10^{-6} at 0°, 0.75×10^{-6} at 18°, and 0.80×10^{-6} at 25° are in close agreement with the experimental results obtained in widely separated laboratories.

A redetermination of the ionisation constant of carbonic acid has given $k=2.24\times10^{-7}$ at 0°, 3.12×10^{-7} at 18°, and 3.50×10^{-7} at 25°. The heat of ionisation, calculated from these numbers, is in close agreement with the value afforded by Thomsen's thermochemical measurements (−2800 cal.).

From observations on the conductivity of dilute solutions of sodium and calcium hydrogen carbonates, the mobility of the HCO_3' ion at 25° = 46.2. From this number the limiting equivalent conductivity of carbonic acid is calculated to be 264 at 0°, 354.0 at 18°, and 393.4 at 25°.

New determinations of the carbon dioxide content of the atmosphere support older results in showing that the deviations from the average of 0.035 vol. % are probably less than 10%, and by taking this average value and combining it with recent data for the solubility of carbon dioxide in water, the conductivity values recorded above have been calculated. The close agreement with the conductivity of pure water in contact with the air shows that conducting impurities other than carbonic acid are not present in appreciable quantity. H. M. D.

The Electrical Phenomena at the Surface of Separation of Aqueous Solutions and Insulators. G. BORELIUS (*Ann. Physik*, 1916, [iv], **50**, 447—471).—The measurements of the difference of potential at the surface of contact of solid paraffin with aqueous solutions (A., 1915, ii, 211) have been extended and the previous results confirmed.

In a theoretical discussion of the results obtained for a large number of electrolytes in varying concentration, it is pointed out that the three following processes may be the primary cause of the electrical phenomena: (1) the contact substance may pass into solution in the form of molecules or ions, (2) the electrolyte (or its ions) may distribute itself between the water and the insulator, (3) the electrolyte (or its ions) may be adsorbed at the surface of the insulator. When the data are examined in reference to these hypothetical processes, it is found that the third leads to equations for the contact difference of potential which are in better agreement

with the experimental results than are the equations which are derived on the assumption that the first or the second process is responsible for the electrical effect.

Incidentally, a comparison is made between the results of the static measurements of the potential difference and those which have been obtained by Ellis (A., 1912, ii, 13, 1036) and Powis (A., 1914, ii, 137, 183) from observations on the electrical cataphoresis of drops of paraffin oil. H. M. D.

Improved Hasselbalch Hydrogen Electrode and a Combined Tonometer and Hydrogen Electrode, together with Rapid Methods of Estimating the Buffer Value of Blood. J. F. McClendon and C. A. Magoon (*J. Biol. Chem.*, 1916, **25**, 669—681).—The new hydrogen electrode has two compartments, the smaller of which contains the electrode proper. Hydrogen is shaken with a portion of the solution in the large compartment, and then passed through a large stop-cock into the smaller compartment containing another portion of the solution, where the reading is made. Since the hydrogen is brought to an equilibrium with the first portion of the solution, it does not appreciably remove carbon dioxide from the second portion, and in this way the danger of loss of carbon dioxide during transfer of the solution is eliminated. By means of this instrument it is found that the hydrion concentration of serum is the same as that of defibrinated blood prepared from the same source and without loss of carbon dioxide.

The new combined tonometer and electrode cell is a modification of that described by Peters (*Proc. Physiol. Soc.*, 1914, vii–viii; *J. Physiol*, **48**).

For facilitating the estimation of the buffer values of blood and serum, charts have been constructed with curves showing the change of p_H with change of carbon dioxide tension. Since the p_H of arterial blood both in health and disease is remarkably constant (about 7·5), the curve in the chart corresponding with any sample of blood or serum may be found by a single observation of the alveolar carbon dioxide tension or of the p_H at a known carbon dioxide tension. H. W. B.

Hydrogen Electrode Potentials of Phthalate, Phosphate and Borate Buffer Mixtures. William Mansfield Clark and Herbert A. Lubs (*J. Biol. Chem.*, 1916, **25**, 479—510).—The authors discuss the evaluation of the $N/10$-potassium chloride–calomel electrode in terms of the "normal hydrogen electrode," the conclusion being that in biochemical work the $N/10$-potassium chloride–calomel electrode should be given the provisional and somewhat arbitrary value 0·3385 between 18° and 30° when referred to the potential of the "normal hydrogen electrode."

The hydrogen electrode potentials of the following mixtures have been studied at 20°, the concentration of the first component being maintained at $M/20$ in all cases: potassium hydrogen phthalate and hydrochloric acid, potassium hydrogen phthalate and sodium hydroxide, potassium dihydrogen phosphate and sodium hydroxide, boric

acid + potassium chloride and sodium hydroxide, boric acid and sodium hydroxide, and, at 25°, potassium chloride and hydrochloric acid. By applying the barometric correction and the above value of the $N/10$-calomel electrode, the p_H values of the various mixtures are calculated and the compositions given which furnish mixtures differing by intervals of 0·2 p_H for use as comparison solutions in the colorimetric estimation of hydrion concentrations. It is maintained that the system of "buffer" mixtures described is somewhat more simple to prepare and easier to standardise than the systems in common use. H. W. B.

The Use of Partly Neutralised Mixtures of Acids as Hydrion Regulators. E. B. R. PRIDEAUX (*Proc. Roy. Soc.*, 1916, [*A*], **92**, 463—468. Compare A., 1915, ii, 677).—When hydrion regulators are prepared from partly neutralised acids, the most suitable degree of neutralisation is that for which $[H^{\cdot}] = k$, the ionisation constant of the acid. In this region, the neutralisation curve, obtained by plotting $\log[H^{\cdot}]$ or $p_{H^{\cdot}}$ against the quantity of neutralised acid, is approximately a straight line with only a slight inclination to the axis of abscissæ. A dibasic acid affords two such regions corresponding with the first and second stages in the ionisation, and each of the flat portions of the curve covers a range of 2 expressed in terms of $p_{H^{\cdot}}$. As a rule the intermediate portions of the curve are inflected, and if the ratio of the two ionisation constants is large, the partly neutralised acid solutions corresponding with this intermediate region are unsuitable for use as hydrion regulators. On the other hand, if the ionisation constants of a polybasic acid do not differ very greatly, the curve of neutralisation is not markedly inflected, and for this reason partly neutralised citric acid solutions in combination with solutions containing citric and hydrochloric acids may be employed for the production of regulator mixtures covering the range $p_{H^{\cdot}} = 1$ to 6. Other regulator mixtures have, however, marked inflections, and in consequence it is necessary to employ several of these if a wide range of $[H^{\cdot}]$ is required.

In view of the utility of a mixture which would cover a wide range of $[H^{\cdot}]$, potential measurements have been made with partly neutralised mixtures of boric, acetic, and phosphoric acids. Such a mixture may be considered to contain five acids with gradually diminishing ionisation constants, namely, H_3PO_4, $k = 1{\cdot}1 \times 10^{-2}$; $CH_3{\cdot}CO_2H$, $k = 1{\cdot}8 \times 10^{-5}$; H_2PO_4', $k = 2 \times 10^{-7}$; H_3BO_3, $k = 1 \times 10^{-9}$; HPO_4'', $k = 3 \times 10^{-12}$. A solution containing the three acids in equimolar proportions undergoes changes in $[H^{\cdot}]$ on partial neutralisation which correspond with a linear relation between $p_{H^{\cdot}}$ and the percentage of total acid neutralised. If this percentage is R, this relation may be expressed by the equation $p_{H^{\cdot}} = 2{\cdot}3 + (R - 10)0{\cdot}1144$, in which $R = 4x$ and x is the number of c.c. of $0{\cdot}2N$-alkali added to 25 c.c. of $0{\cdot}2N$-acid before the acid solution is diluted to 50 c.c. The formula holds good with considerable accuracy for values of R between 10 and 90, and covers the range $p_{H^{\cdot}} = 2{\cdot}3$ to $p_{H^{\cdot}} = 11{\cdot}5$.

The partly neutralised mixture of boric, acetic, and phosphoric acids has a further advantage over many other regulator mixtures in that it enables the interval $p_{H^{\cdot}} = 7{\cdot}5$ to $8{\cdot}3$ to be reproduced as easily as any other portion of the range. H. M. D.

Electrolytic Dissociation Theory. NILRATAN DHAR (*Zeitsch. Elektrochem.*, 1916, **22**, 245—252).—A theoretical paper in which the position of the electrolytic dissociation theory is critically discussed in the light of recent work. The author is of the opinion that the theory is more, rather than less, firmly established by modern investigations. J. F. S.

Relations between the Constants of Dibasic Acids and of Amphoteric Electrolytes. ELLIOT QUINCY ADAMS (*J. Amer. Chem. Soc.*, 1916, **38**, 1503—1510).—The ionisation of a dibasic acid, HAH, in which the two ionisable hydrogens are distinguished by being written respectively before and after the symbol A of the negative radicle, is represented by the equations: $K_1 = [H^{\cdot}][AH']/[HAH]$; $K_2 = [H^{\cdot}][HA']/[HAH]$; $K_3 = [H^{\cdot}][A'']/[HA']$; $K_4 = [H^{\cdot}][A'']/[AH']$. Expressions for the first and the second dissociation constants, K' and K'', as ordinarily defined, are therefore given by the equations $K' = K_1 + K_2$ (I) and $K'' = K_3K_4/K_3 + K_4$ (II). The simplest case is that in which the acid is symmetrical, and the hydrogens are independent of each other's ionisation; then $K_1 = K_2 = K_3 = K_4$ and $K' = 2K$ and $K'' = \frac{1}{2}K$. For independently ionisable hydrogens in an unsymmetrical acid, $K_3 = K_1$ and $K_4 = K_2$, and equation (II) becomes $K'' = K_1K_2/K_1 + K_2$. The most complex case occurs when the acid is unsymmetrical, and the hydrogens are not sufficiently separated to ionise independently. In this case it can be shown that $K'/K'' > 4$ (III). For a tribasic acid it may be shown in similar fashion that the limiting ratio between successive constants is 3; indeed, the calculation may be made for an acid with any number of ionisable hydrogens. Numerous examples are quoted from the literature in support of the preceding relations; in the cases of phenolphthalein and crystal-violet the value of K'/K'' is very near the limiting value 4, and Chandler has shown (A., 1908, ii, 467) that the same limit is approached in dibasic organic acids at high concentrations.

Relations (I) and (III) apply directly to amphoteric electrolytes if the constant of the basic part of the molecule is expressed in terms of hydrogen-ion concentration. For example, aminoacetic acid has $K_A = 1{\cdot}8 \times 10^{-10}$ and $K_B = 2{\cdot}8 \times 10^{-12}$; in the author's notation these become $K'' = 1{\cdot}8 \times 10^{-10}$ and $K' = 3{\cdot}7 \times 10^{-3}$, showing that aminoacetic acid is at once a base nearly as strong as methylamine ($K = 2{\cdot}4 \times 10^{-11}$) and an acid stronger than monochloroacetic acid ($K = 1{\cdot}6 \times 10^{-3}$). C. S.

The Energy Changes of Binary Systems. VIII. The Connexion between the Heats of Mixing and the Vapour Pressure Curves of Binary Systems. ROBERT KREMANN (*Monatsh.*, 1916, **37**, 369—389. Compare this vol., ii, 471).—In a

theoretical discussion of the interpretation of the vapour-pressure curves of binary mixtures, it is pointed out that vapour pressures in agreement with those calculated by the simple mixture rule are only to be expected when no heat change accompanies the mixing of the components. For normal mixtures of normal components, mixing is accompanied by heat absorption, and the vapour pressures of mixtures are consequently greater than those calculated according to the mixture rule. The recognition of this relation is of essential importance in the quantitative determination of the constitution of binary mixtures from vapour-pressure data. The usual assumption, that the deviation of the experimental vapour pressure curve from the straight line corresponding with the mixture rule affords a measure of the disturbance due to association or compound formation, is obviously not in agreement with the behaviour of normal mixtures which give a positive vapour-pressure curve.

H. M. D.

The Vapour Pressures of Binary Liquid Mixtures. Kinetic Theory based on Dieterici's Equation. FRANK TINKER (*Phil. Mag.*, 1916, [vi], **32**, 295—302).—If the pressure due to the molecular bombardment of either side of unit plane immersed in a liquid is termed the liquid pressure, it is shown that for binary mixtures which show no change in volume on mixing, the total liquid pressure (π) of the mixture may be calculated from the liquid pressures of the components by the mixture rule as expressed by the equation $\pi = \pi_1' + \pi_2' = x\pi_1 + (1-x)\pi_2$, where π_1 and π_2 are the liquid pressures of the pure components, π_1' and π_2' the partial liquid pressures of the components in the mixture containing these in the molar ratio $x:(1-x)$.

By application of the Dieterici equation of state to a binary mixture, it is shown that the relation between the total vapour pressure (p) of a mixture and the vapour pressures p_1 and p_2 of the pure components may be expressed by the equation

$$p = \{xp_1 + (1-x)p_2\}(1 - \delta L/RT),$$

or if p_0 is the vapour pressure of the mixture calculated from the simple mixture rule, by the equation $p = p_0(1 - \delta L/RT)$, in which δL is the excess of the molecular heat of vaporisation of the mixture over the latent heat calculated according to the mixture rule.

According to this the variation of the total vapour pressures for the straight line law is mainly determined by abnormalities in the latent heat of vaporisation.

The general soundness of the equation is shown indirectly by reference to surface tension data which are known to bear a close relation to the heats of vaporisation.

H. M. D.

The Dissociation Tensions of Certain Hydrated Chlorides and the Vapour Pressures of their Saturated Solutions. I. H. DERBY and VICTOR YNGVE (*J. Amer. Chem. Soc.*, 1916, **38**, 1439—1451).—Measurements of the vapour pressures of certain hydrated salts and of their saturated solutions have been made by the use of an isoteniscope. The recorded data relate to the vapour

pressures of $MgCl_2,6H_2O$, $CuCl_2,2H_2O$, $CoCl_2,6H_2O$, $NiCl_2,6H_2O$, and $NiCl_2,4H_2O$, and also of the saturated solutions of $MgCl_2,6H_2O$, $MgCl_2,4H_2O$, $CuCl_2,2H_2O$, $CoCl_2,6H_2O$, $CoCl_2,2H_2O$, $NiCl_2,6H_2O$, and $NiCl_2,4H_2O$. The curves indicate that the hexahydrate of nickel chloride is transformed into the tetrahydrate at 36·25°. It is also pointed out that the pressure curves for the saturated solutions tend to become parallel to the temperature axis in the neighbourhood of the transition points. In the case of magnesium chloride hexahydrate the curve is even retroflex. H. M. D.

An Adiabatic Calorimeter. FARRINGTON DANIELS (*J. Amer. Chem. Soc.*, 1916, **38**, 1473—1480).—A form of calorimeter is described, in which it has been found possible to keep the average difference of temperature between the calorimeter and its jacket smaller than 0·01°, if the rate of change of temperature is not too rapid. The junctions of a copper-constantan thermocouple are immersed in the calorimeter and in the water-jacket, any difference of temperature being indicated by a galvanometer deflection. As soon as the galvanometer registers a difference in temperature, a current is made to pass through the water-jacket, and this current is then cut off as soon as the spot of light returns to its zero position. The electrolytic heating of the jacket is combined with efficient stirring of the contents of both the calorimeter and the jacket. By means of a selenium cell it has been found possible to make the temperature control automatic.

Special advantages are claimed for a calorimeter of this type for high temperature observations, for reactions of small velocity, and for thermal measurements in which large differences of temperature are involved. H. M. D.

The Stability of Diatomic Molecules, the Heat of Dissociation and the Relation of these to Electro-chemical Theory. F. RICHARZ (*Ann. Physik*, 1916, [iv], **50**, 229—232).—With reference to Kossel's paper (this vol., ii, 243) on the formation of molecules, it is pointed out that the conclusions relative to the connexion between the stability and heat of dissociation of diatomic molecules must be considered in relation to the ionic or non-ionic character of the dissociation. H. M. D.

The Thermochemistry of Silicon; Heat of Combination of Silica with Water. W. G. MIXTER (*Amer. J. Sci.*, 1916, [iv], **42**, 125—132).—The thermochemistry of silica compounds is reviewed. According to experiments in which preparations of silica containing varying quantities of water were dissolved in a 22% solution of hydrofluoric acid, it has been found that the combination of silica with water is accompanied by little or no heat change. The most probable value for the heat of formation of silica from crystalline silicon is given as 191 Cal. H. M. D.

Volume Changes of Amalgams. J. WÜRSCHMIDT (*Ber. Deut. physikal. Ges.*, 1914, **16**, 799—812. Compare A., 1913, ii, 101, 1027).—Further observations, relative to the changes in volume

which are shown by bismuth amalgams when the temperature is raised have led to the conclusion that the anomalies are due to the existence of two modifications of bismuth with a transition temperature at 75°. The β-form, which is stable below 75°, is transformed into the α-form with a considerable diminution in volume.

Repeated heating and cooling of the amalgam results in the gradual disappearance of the contraction which is exhibited by the freshly prepared amalgam at or above 75°, and this is found to be due to the gradual segregation of the components of the alloy. If the amalgam is strongly heated, the anomalies characteristic of the freshly prepared amalgam reappear. H. M. D.

Further Determinations of Direct Osmotic Pressures. The EARL OF BERKELEY and E. G. J. HARTLEY (*Proc. Roy. Soc.*, 1916, [*A*], **92**, 477—492).—In continuation of previous experiments (*Phil. Trans.*, 1906, [*A*], **206**, 481; 1909, [*A*], **209**, 177), the results of direct measurements of the osmotic pressures of aqueous solutions are recorded.

The new data for solutions of sucrose are compared with the results obtained by Morse and his collaborators, and this comparison shows that the authors' values for the osmotic pressures of the more dilute solutions are smaller to an extent which cannot be accounted for by the probable errors of the experiments. The discrepancies are shown by the following numbers, which give the weight of sucrose dissolved in 100 grams of water and the percentage difference between the osmotic pressures: 3·39, 8·2%; 10·2, 2·4%; 20·5, 1·2%; 30·6, 0·2%; 33·9, 0·1%. According to these figures the percentage deviation increases rapidly with the dilution.

Values for the osmotic pressures of solutions of α-methyl glucoside, *iso*dulcitol, and α-tetramethyl ferrocyanide, and also of various inorganic and organic salts, are also recorded.

The values obtained for magnesium ferrocyanide suggest that the substance is partly associated, and evidence of the formation of associated molecules is also shown by the results for magnesium sulphate, magnesium chromate, and zinc sulphate. Although these salts are undoubtedly ionised, the observed osmotic pressures are smaller than those calculated from the simple gas equation.

A simple dynamic method for the approximate measurement of small osmotic pressures is described, which involves a comparison of the rates of flow of water through the semipermeable membrane when solutions of approximately the same molar concentration are brought into contact with the opposite side of the membrane. If the rate of flow for the standard substance (molecular weight M) at concentration C is R, and the corresponding quantities for a second substance are M', C', and R'; then $M'R'/C' = MR/C$, from which M' can be calculated. The accuracy of this method is about 2%, but it is considered that the experimental error might be reduced with a specially designed form of apparatus. H. M. D.

Solubility. JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1916, **38**, 1452—1473).—On the assumption that Raoult's vapour pres-

sure law is applicable to solutions, it is shown that simple expressions may be derived for the solubility of gases and solids in liquids.

If the saturated solution contains n_1 mols. of solute (X_1) and n_2 mols. of solvent (X_2), then the relation between the pressure of the gas (p_1) and the molar concentration of the solution is given by $p_1 = k \, . \, n_1/n_1 + n_2$. The significance of the constant k is made clear by putting $n_2 = 0$, when k becomes equal to the vapour pressure (P_1) of the liquid solute. If the temperature of the solution is higher than the critical temperature of the gas, the vapour pressure P_1 has no real significance, and on this account the term fugacity may be more conveniently employed to describe the property in question. Its numerical value would correspond with the extrapolation of the vapour-pressure curve of the liquid in question.

In the case of saturated solutions of solids in liquids, if P_1 and P_1' represent the fugacities or vapour pressures of the liquid and solid solute respectively, then the molar concentration of the saturated solution is given by $n_1/n_1 + n_2 = P_1'/P_1$. The ratio P_1'/P_1 is given by the equation $\log P_1'/P_1 = -L_0/4{\cdot}58T + \Delta S \, . \log T/1{\cdot}99 + I$, in which L_0 is the molar heat of fusion at absolute zero, ΔS is the difference in the heat capacity of the liquid and solid forms, and I is an integration constant, the value of which is obtained by making T equal to the melting point when $\log P_1'/P_1 = 0$.

Although Raoult's law is approximately true for many liquid mixtures, experiment shows that many other mixtures deviate largely from the requirements of this generalisation. The attempts to explain these deviations by chemical combination and change in the degree of association of the components are not considered very satisfactory, and the author gives preference to the van der Waals's equation as a basis of explanation, a method which has already been discussed in particular by van Laar.

The validity of Raoult's law is probably limited to mixtures in which the forces acting between the molecules are not very different from those acting between the molecules of the pure liquids. It is suggested that approximate equality of the internal pressures affords a criterion for the required similarity in the molecular environment. In most cases the order in which liquids are arranged according to the internal pressures agrees well with the order according to the critical pressures, which is not surprising, since according to van der Waals's theory the critical pressure is given by $8a/27b^2$ and the internal pressure by a/v^2, and it is well known that b and v are related in a simple manner.

A further factor which has great influence on the properties of a liquid and its mixtures is the so-called polarity. Molecules which are electrically polar will tend to form associated groups, and this polarity hence gives rise to increased internal pressure and surface tension. In consequence of the orientation of the molecules in an electric field, the polarity is associated with a high dielectric constant. Examples of polar liquids are furnished by the ionising solvents, and still greater polarity is shown by molten salts which have been shown to be characterised by abnormally high values of surface tension and association factor. The molten metals prob-

ably furnish examples of extreme polarity, this again being associated with high electrical conductivity and surface tension.

Deviations from Raoult's law are to be expected in all mixtures where one or both of the components are polar, and also for mixtures of non-polar liquids with different internal pressures. These deviations modify the solubility relations in the sense that the solubilities are greater when the deviations are negative and smaller when the deviations are positive. The deviations are positive for mixtures of non-polar liquids of different internal pressure, and also for mixtures of a polar and a non-polar liquid. For mixtures of polar liquids the deviations may be either positive or negative, being usually positive when there is a considerable difference in the polarity and negative when both are highly polar.

Experimental data relating to the solubility of gases in liquids, the miscibility of liquid pairs, and the solubility of solids in liquids are discussed in relation to the views put forward, and these would seem to show that the solubility is very largely influenced by the nature of the molecular environment, that is to say, by the magnitude of the internal pressure and the polar character of the molecules. H. M. D.

A Class of Solubility Elevations. HANS VON EULER and ERIK LÖWENHAMN (*Zeitsch. Elektrochem.*, 1916, **22**, 254—255).—An addendum and correction to the authors' previous paper (this vol., ii, 476). It is pointed out that the solubility increases of benzoic acid and salicylic acid given in the previous paper refer, not to solutions in benzene, as stated in the paper, but to a mixture of toluene and benzene. This correction does not affect the conclusions drawn in the paper. New determinations at 18° show that 1 litre of benzene dissolves 0·59 gram-molecule of benzoic acid, and 0·038 gram-molecule of salicylic acid when these substances are dissolved alone in benzene, but when both are added together to the benzene, 0·60 gram-molecule of benzoic acid and 0·145 gram-molecule of salicylic acid dissolve. J. F. S.

A New Method for the Purification of Colloidal Solutions. G. WEGELIN (*Kolloid Zeitsch.*, 1916, **18**, 225—237).—The method depends on ultra-filtration by the use of a collodion membrane. The apparatus consists of a funnel-shaped vessel containing the colloidal solution to be purified, this vessel being closed near the top by the ultra-filter, whilst water under pressure may be introduced through the lower narrow end of the funnel, the rate of flow being regulated by means of a tap. The aqueous solution which passes through the collodion filter is run off into collecting vessels, and may be examined from time to time in order to gauge the progress of the purification process. It is essential that the flow of liquid should be upwards, for preliminary experiments in which the colloidal solution was placed above the ultra-filter showed that the colloidal particles under the continued influence of gravity and of the current of liquid tended to accumulate on the upper surface of the membrane to such an extent that this rapidly became impermeable to the wash water.

For the production of suitable filters, the author recommends the use of solutions of collodion in acetic acid. The solution, containing from 7·5 to 15% of collodion, is spread out in a uniform, thin layer on a glass plate, and the film subjected to the action of running water for five to ten minutes. The porosity varies very considerably with the concentration of the collodion solution, a membrane prepared from a 7·5% solution having been found to be about ten times as porous as that prepared from a 15% solution. The membranes may not be dried, and even when kept under water it is found that ageing takes place.

The apparatus has been found to give satisfactory results in the purification of colloidal solutions of antimony, arsenic, and molybdenum sulphide, gold, palladium, silicic acid, ferric hydroxide, aluminium hydroxide, vanadium pentoxide, blood serum, and egg-albumin.

The apparatus may also be employed for the preparation of colloidal solutions containing particles of determinate size, for the concentration of dilute solutions of colloids, for measurements of the size of colloidal particles, and for the purification of precipitated substances which cannot be easily washed by the usual filtration methods. H. M. D.

The Coagulation of Colloidal Arsenious Sulphide by Electrolytes and its Relation to the Potential Difference at the Surface of the Particles. FRANK POWIS (T., 1916, **109**, 734—744).—Coagulation experiments with a colloidal solution of arsenious sulphide have shown that there is no definite concentration of electrolyte above which immediate coagulation occurs and below which no coagulation takes place. According to observations made with barium chloride as coagulating electrolyte, the limiting concentrations corresponding with rapid and with no coagulation are, however, fairly close, the recorded values being 0·8 and 0·3 millimol. per litre respectively. It is suggested that the presence of particles of different sizes is the probable cause of the observed range in the coagulating concentration, for earlier experiments have shown that large particles coagulate more easily than small particles.

In coagulation experiments of this kind it is essential that the method of mixing the electrolyte and colloid solutions should be such as to eliminate the possibility of initial disturbances, and regard must be paid to the effect of agitation of the solution.

Measurements by a cataphoretic method of the potential difference between the colloidal particles and solutions of various electrolytes, the concentrations of which were adjusted to the lowest value at which rapid coagulation occurred, gave results which show that the potential difference for potassium, barium, and aluminium chlorides and for thorium nitrate, in all cases exceeds 0·02 volt. The coagulation concentration is therefore not that at which the potential difference becomes zero (the *iso*electric point), and in this respect the results confirm the conclusion drawn by the author from similar observations on oil-water emulsions (compare A., 1914, ii, 137, 183) The value of the critical potential is about 0·025 volt

for barium chloride, aluminium chloride, and thorium nitrate, but is distinctly higher for potassium chloride (0·044 volt), and it is suggested that this may be due to a superposed salting-out effect.

In regard to the coagulation concentrations of the four electrolytes, it is found that these do not form a geometric series, such as has been frequently associated with the coagulating powers of ions of different valency. H. M. D.

Protective Colloids. IV. Linseed as Protective Colloid. 2. Colloidal Gold. A. GUTBIER, J. HUBER, and E. KUHN (*Kolloid Zeitsch.*, 1916, **18**, 263—273. Compare this vol., ii, 303, 476).—The colloidal substances extracted from linseed have been examined with reference to their protective action on colloidal gold prepared by the reducing action of hydrazine hydrate, formaldehyde, sodium hyposulphite, and phenylhydrazine on gold chloride solution in presence of the colloid extract and chloroform. Experiments demonstrating the protective action are described in detail.

By evaporation of the solutions in an exhausted desiccator over concentrated sulphuric acid, solid gold colloids may be obtained containing more than 50% of gold, which dissolve completely in warm water. H. M. D.

Aqueous Solutions of Carbonic Acid. ROBERT STROHECKER (*Zeitsch. Nahr. Genussm.*, 1916, **31**, 121—160).—It has been shown previously that the neutralisation of carbonic acid requires an appreciable amount of time, and experiments are described in which the reaction has been investigated from the kinetic point of view. The time factor is readily observed if 25 c.c. of a solution saturated with carbon dioxide is diluted to 200 c.c. and added to 7 c.c. of $0{\cdot}1N$-sodium hydroxide solution containing 5 drops of a 1% alcoholic phenolphthalein solution. For some time after mixing the red colour persists, but it gradually fades and the solution ultimately becomes colourless.

In the detailed investigation of this neutralisation process dynamic measurements were made in which solutions of carbonic acid were mixed with solutions of sodium, potassium, ammonium, and tetraethylammonium hydroxide, and further with solutions of sodium carbonate, and of sodium carbonate in presence of sodium hydrogen carbonate. The concentrations of the reacting substances were varied relatively and absolutely, and the influence of temperature was determined by measurements at 4° and 14°. The progress of the reaction was ascertained by colorimetric comparison of the solution under investigation with standard solutions of known hydrogen-ion concentration, to which a suitable indicator had been added. The most suitable indicators were found to be tetrachlorophenol, changing very sharply at $[H^{\cdot}]=10^{-8}$, methyl-red, which also changes sharply at $[H^{\cdot}]=10^{-6\cdot8}$, and α-naphtholphthalein, which shows a well-defined series of colours extending over a wide range of hydrogen-ion concentration.

The results obtained show that the time required for neutralisation diminishes with increase in the concentration of the acid and

increases when the concentration of the alkali is increased. When the concentrations of acid and alkali are altered in the same ratio the time remains the same. Sodium, potassium, and tetraethylammonium hydroxides are very nearly identical in their behaviour, but when ammonia is employed for neutralisation, the time required is very much longer. When equivalent solutions of sodium hydroxide and sodium carbonate are compared, it is found that the neutralisation interval is much greater in the case of the carbonate.

The mechanism of the reaction seems to vary with the stage of the neutralisation process, and although the results cannot be satisfactorily interpreted in terms of the equations for either a unimolecular or a bimolecular reaction, it seems very probable that the time factor is mainly to be attributed to the relative slowness of the reaction $CO_2 + H_2O \longrightarrow H_2CO_3$.

On the assumption that this is the time reaction, experiments have been made to determine the proportion of the total dissolved carbon dioxide which is present in the hydrated form. These experiments show that a 0·008544 molar solution of carbon dioxide contains 0·56% in the hydrated form. This number is employed to calculate the true ionisation constant of carbonic acid. Whereas, according to conductivity data, the apparent ionisation constant at 4° is $k = 2{\cdot}2 \times 10^{-7}$, the true ionisation constant is $k = 4{\cdot}4 \times 10^{-4}$.

If carbonic acid is regarded as hydroxyformic acid, this higher value of the ionisation constant harmonises quite well with the relations which have been found to obtain between the constants of the fatty acids and the corresponding hydroxy-substituted acids.

Attention is drawn to the necessity of taking into account the velocity of neutralisation of carbonic acid in the estimation of this in potable and other waters. For accurate results, Winkler's process should be used, the measured sample of water being added to an excess of standard alkali with the addition of barium chloride, the stoppered vessel being kept for one hour before the excess alkali is estimated by titration with standard acid. H. M. D.

Reactivity of the Halogens in Organic Compounds. Part IX. Interaction of Alkalis and Alkali Bromoacetates and Bromopropionates in Ethyl-Alcoholic Solution. George Senter and Henry Wood (T., 1916, **109**, 681—689. Compare T., 1915, **107**, 1070).—In the earlier publication the action of alkalis on alkali bromoacetates and bromopropionates in methyl alcohol and mixtures of methyl alcohol and water was discussed, and the present paper gives the results of a similar investigation, using ethyl alcohol. On account of the sparing solubility of sodium bromoacetate in ethyl alcohol, it was found impossible to measure the velocity of the reaction between sodium bromoacetate and sodium ethoxide.

The reaction with sodium bromoacetate in aqueous-ethyl alcoholic solution is pseudo-bimolecular, giving, in any one solution, velocity constants in good agreement with the assumption of a bimolecular reaction, but with alteration of the initial concentrations of the reacting substances the velocity-coefficients increase

more rapidly than the concentration of the sodium ethoxide. The displacement of bromine occurs about six times as fast in 90% ethyl alcohol as in 90% methyl alcohol (compare Hecht, Conrad, and Brückner, A., 1890, 4, 1046; Kremann, A., 1905, ii, 307). For the determination of the proportion of ethoxy-acid in the final product by the Zeisel method a modification of Hewitt and Moore's apparatus (T., 1902, **81**, 318) was used with excellent results, and it was found that up to 40% of alcohol the proportion of ethoxy-acid formed is greater than that of the alcohol present in the solution.

With sodium bromopropionate the action of ethyl alcohol is comparable in speed with that of sodium ethoxide, the rate of displacement of bromine attaining a maximum in mixtures containing about 25% of alcohol. D. F. T.

The Walden Inversion. III. The Kinetics and Dissociation Constant of Phenylbromoacetic Acid. GEORGE SENTER and STANLEY HORWOOD TUCKER (T., 1916, **109**, 690—697).—The present communication deals with the chemical kinetics of the displacement of bromine by hydroxyl in *r*-phenylbromoacetic acid and sodium phenylbromoacetate, the method of experiment being similar to that already described in the case of phenylchloroacetic acid (Senter, T., 1915, **107**, 908).

The dissociation constant of phenylbromoacetic acid at 25° was found to be 0·0035, when concentrations are expressed in mols. per litre. A redetermination of the constant for phenylchloroacetic acid (compare *loc. cit.*) gave the value 0·0044. Measurements of the velocity of hydroxylation of phenylbromoacetic acid ($N/40$) by water at 25° and 40·4° gave unimolecular "constants" which decreased in value as the reaction proceeded. This decrease was proved to be due to the accumulation of hydrobromic acid in the system, as was shown by the fact that in the presence of $N/5$-hydrobromic acid the constants were much smaller and showed no decrease during the course of the reaction. This result is explained by the fact that both the undissociated acid and the anion react with water, the latter much more quickly (about 120 times faster) than the former. As hydrobromic acid is produced in the system the dissociation of the phenylbromoacetic acid is more and more suppressed, with a consequent decrease in the velocity constant; in the presence of a large excess of hydrobromic acid the alteration of the dissociation during the reaction is practically negligible, and a satisfactory constant is obtained, although both the undissociated phenylbromoacetic acid and the anion are undergoing hydroxylation. The temperature-coefficient of hydroxylation has the high value 4·0.

The hydroxylation of sodium phenylbromoacetate in $N/40$-aqueous solution at 25° and 40·4° is a unimolecular reaction, the temperature-coefficient being 3·65. The reaction goes slightly faster in the presence of $N/40$-sodium hydroxide, but a further increase in the concentration of the sodium hydroxide to $0·312N$ has no accelerating effect. It follows that the action of hydroxyl ions on sodium phenylbromoacetate is quite negligible in comparison with

that of water, as has already been found for sodium phenylchloroacetate.

Bromine is displaced from phenylbromoacetic acid and its salts about ten times as fast as chlorine is displaced from phenylchloroacetic acid and its compounds under equivalent conditions. Approximately the same ratio has previously been obtained in the investigation of other halogen-substituted acids. T. S. P.

Saponification of the Esters of the Pyrrolecarboxylic Acids at a Temperature of 50°. G. KORSCHUN and A. GOUNDER (*Bull. Soc. chim.*, 1916, [iv], **19**, 221—242).—The authors have amplified and extended their work on the saponification of the pyrrolecarboxylic ethyl esters (compare this vol., i, 606). The replacement of the hydrogen atom attached to the nitrogen atom in ethyl 2:5-dimethylpyrrole-3-carboxylate by the carbamido-group produces a diminution in the velocity of saponification. A further replacement of the hydrogen atom in position 4 in this second ester by a methyl group produces a further diminution in the velocity of saponification of the ester. The replacement of the methyl group in position 2 in ethyl 1-carbamido-2:5-dimethylpyrrolecarboxylate by a phenyl group produces a rise in the velocity of saponification of the ester. Starting with ethyl 1:2:4:5-tetramethylpyrrole-3-carboxylate, the velocity of saponification is increased by replacing the methyl group in position 5 by an acetyl group. Full numerical data are given in the original paper. W. G.

The Age of the Alchemists J. I. and I. Hollandus. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1916, **40**, 605).—Historical. J. I. Hollandus died about 1610, whilst Isaak Hollandus was still alive at that date. Their work first appeared in print about 1600.
G. F. M.

A Non-Spattering Wash-bottle. F. C. CLAPP (*J. Amer. Chem. Soc.*, 1916, **38**, 1502—1503).—The nozzle is made to remain full of water by means of an arrangement in which the portion of the delivery tube inside the wash-bottle is surrounded by a wider tube in which the level of the water is raised slightly above the level of the lip of the nozzle. H. M. D.

Inorganic Chemistry.

Hydrogen from Formates and from Carbon Monoxide. M. G. Levi and A. Piva (*Ann. Chim. Applicata*, 1916, **5**, 271—301).—Further experiments have been made on the decomposition of the formates (compare A., 1914, i, 480) and investigations made on the conditions of formation of formates and in

general on the conditions of reaction between carbon monoxide and alkali.

The presence of calcium hydroxide lowers the temperature at which calcium formate decomposes from 375° to 280° for an equimolecular mixture and to 260° for the mixture $(HCO_2)_2Ca + 2Ca(OH)_2$. As regards the gases generated, the presence of lime causes (1) the proportion of carbon dioxide to diminish gradually to zero, (2) that of carbon monoxide to decrease markedly, and (3) that of hydrogen to increase from a maximum of 45 c.c. for 1 gram of the pure formate to 220 c.c. for 1 gram of formate in presence of the hydroxide, the proportion of hydrogen in the gas formed rising from 35% to 93%. Assuming that the reaction is expressible by the equation $(HCO_2)_2Ca + Ca(OH)_2 = 2CaCO_3 + 2H_2$, 1 gram of the formate should be capable of yielding 344 c.c. of hydrogen. The small proportion of methane formed disappears in presence of large amounts of lime.

With reference to the action of carbon monoxide on lime or sodium hydroxide or soda lime, either dry or in presence of water vapour, the results of the author's experiments point to the following conclusions: (1) With pure lime, carbon monoxide gives formate at 250—300° and carbonate and hydrogen above 300°; the formation takes place moderately slowly and to a much less extent than with sodium hydroxide, since, in the fundamental equilibrium between carbon monoxide and water, $CO + H_2O \rightleftharpoons H{\cdot}CO_2H$, the lime, being a weak base, exercises only a slight displacement. At 500—600° the formation of hydrogen is almost quantitative, provided always that the elements of water are present. (2) The addition of sodium hydroxide to the lime facilitates the formation of formate, rendering it possible even at 150—200°, and lowers the temperature at which hydrogen is formed, the reaction proceeding in this direction to the extent of 50% at 300°; the presence of the two bases together increases the yield of hydrogen. T. H. P.

The Density of Hydrogen Bromide Gas. Revision of the Atomic Weight of Bromine. E. Moles (*Compt. rend.*, 1916, **163**, 94—97. Compare this vol., ii, 314).—The author has made further determinations of the density of hydrogen bromide gas, prepared by the action of bromine on naphthalene in the cold and on paraffin heated at 200°, the resulting gas being carefully purified in each case. As a mean of thirty-three determinations he now gives the value 3·64442 ± 0·00013 grams as the weight of a normal litre of hydrogen bromide. The weight of a litre of the gas under reduced pressures has been determined, and these results give for the coefficient of compressibility of hydrogen bromide, $1 + \lambda = 1{\cdot}00931$, whence the molecular weight of the gas as compared with oxygen is 80·934; and the atomic weight of bromine, taking hydrogen = 1·008, is 79·926. W. G.

Ozonisation of Liquid Oxygen by Radiation. E. Warburg (*Ber. Deut. physikal. Ges.*, 1915, **17**, 194—197).—Small quantities of ozone are formed by the action of ultra-violet radiation on oxygen

at atmospheric pressure, but since rays of wave-length exceeding $0{\cdot}2\,\mu$ are only slightly absorbed by oxygen under these conditions, it was considered possible that larger quantities might be obtained by the use of liquid oxygen. Experiments made with liquid oxygen and air exposed to the rays emitted by the spark discharge between zinc electrodes show that appreciable quantities of ozone are formed after a short exposure. H. M. D.

Preparation of Free Hydroxylamine from Hydroxylamine Sulphate. OSKAR BAUDISCH and F. JENNER (*Ber.*, 1916, **49**, 1182—1185).—Finely powdered and carefully dried hydroxylamine sulphate is cautiously added to liquid ammonia in a quartz tube, the ammonia is then removed by evacuation, and the free hydroxylamine extracted by alcohol. The operation is attended by grave risks from explosions, but details are given of the manipulation which the authors recommend. J. C. W.

The Constitution of Coal. DAVID TREVOR JONES and RICHARD VERNON WHEELER (T., 1916, **109**, 707—714).—Coal is considered to have been formed from decayed vegetable matter by the action of pressure and heat, the latter not having exceeded a temperature of 300°. The coal is a conglomerate which can be resolved by solvents into "cellulosic" and "resinic" portions (T., 1913, **103**, 1706); thus on extracting coal with pyridine an insoluble, cellulosic residue is obtained, the extract containing a mixture of cellulosic material with resinic compounds, which can be separated by treatment with chloroform, in which the former is insoluble. It is the resinic component of coal which exerts photochemical action on a photographic plate, the effect being due to some slow oxidation; the cellulosic component does not exert this action.

When the cellulosic compounds are submitted to destructive distillation phenols are produced (compare Wichelhaus, A., 1910, i, 868), the formation of these being due to the presence of the furan grouping $\begin{array}{l}\cdot C\cdot CH \\ \;| \\ \cdot C{=}C\end{array}\!\!>O$; there are also present in the cellulosic constituents compounds of which the molecules structurally resemble the carbon molecule (compare Cross and Bevan, *Phil. Mag.*, 1882, [v], **13**, 325; Dimroth and Kerkovius, A., 1913, ii, 774; Pictet and Ramseyer, A., 1911, i, 850), but there is no likelihood of the presence of free carbon.

The resinic compounds are probably of more diverse nature than the cellulosic; they contain alkyl, naphthene, and unsaturated hydroaromatic radicles linked to larger and more complex groupings. Under the influence of pressure the resinic derivatives have become highly polymerised. The oxygenated derivatives present among the resinic compounds are probably cyclic oxides. Free hydrocarbons exist to some extent in the resinic portion of coal (compare Pictet and Ramseyer, *loc. cit.*; Pictet and Bouvier, A., 1915, i, 512), but paraffin hydrocarbons are present only in small quantity.

The outstanding difference between the "petroleum" distilled

from coal and the natural oils is the presence of phenols in the former, and the difference is explicable when the conglomerate character of coal is borne in mind, especially in view of the fact that phenols are distilled only from the cellulosic portions. The absence of phenols from petroleums suggests that the origin of these is of a non-vegetable character. D. F. T.

The Influence of Iron Pyrites on the Oxidation of Coal. THOMAS JAMES DRAKELEY (T., 1916, **109**, 723—733).—A detailed account is given of experiments made to determine the influence of iron pyrites on the oxidation of coal to carbon dioxide and on the absorption of oxygen by the coal. For this purpose a quantitative comparison was made of the oxidation products obtained from (1) pyrites, (2) coal, (3) an artificial mixture of coal and pyrites, (4) ferrous sulphate, (5) a mixture of coal and ferrous sulphate, (6) a mixture of coal and sulphuric acid. The rates at which oxygen was absorbed by these systems were also compared.

The results obtained seem to show that pyrites has a measurable influence in the sense that it increases the rate of oxidation of coal, and its presence may therefore not be entirely disregarded in connexion with the question of the spontaneous ignition of coal. H. M. D.

The Composition and Use of Greek Fire. C. ZENGHELIS (*Compt. rend.*, 1916, **163**, 125—127).—A brief survey of the modern and the ancient literature dealing with the composition and method of using Greek fire. The author considers that Greek fire was, as suggested by Berthelot, based on the addition of nitre to inflammable mixtures, and that the gases produced by the explosive portion propelled the incendiary portion against the enemy. W. G.

The Action of Oxygen on Metallic Oxides at High Temperatures and Pressures. JAROSLAV MILBAUER (*Chem. Zeit.*, 1916, **40**, 587).—When heated for an hour in closed tubes at 480° in oxygen at 12 atm. pressure the majority of metallic oxides remained unchanged. The following exceptions were observed: Potassium oxide was partly converted into peroxide, barium oxide gave barium peroxide, lead oxide was converted into red lead, antimony oxide into the tetroxide, and manganous oxide into the sesquioxide, nickelous and cobaltous oxides contained traces of the nickelic and cobaltic compounds, whilst silver became covered with black crusts, probably of a peroxide, since on treatment with hydrochloric acid chlorine was generated. Intimate mixtures of oxides or carbonates with chromic oxide heated under similar conditions were found in all cases but that of cerium to have been more or less completely converted into the corresponding chromate. With oxides (or carbonates) of the following metals, for example, the product contained the annexed percentage of chromate: Silver, 100%; magnesium, 82·7%; calcium, 56·9%; zinc, 72%; lead, 100%; bismuth, 6·3%; barium, 52·8%. The reaction is apparently in some cases suitable for the technical production of chromic acid salts. G. F. M.

Pure Sodium Chloride. CLIFFORD LOHMANN (*Chem. News*, 1916, **114**, 53).—The following method was employed for separating sodium and potassium chlorides: About 0·5 gram of the salt was dissolved in a little water and treated with 20 drops of a 10% solution of platinum chloride. A few drops of water were added, after which the precipitate was collected and washed five or six times with a mixture of water (2 vols.) and alcohol (1 vol.) and then about six times with a mixture of alcohol and ether. When dry, the precipitate was washed into a weighed platinum crucible with boiling water.

Three samples of sodium chloride, supposed to be chemically pure, were found to contain from 0·45 to 0·57% of potassium chloride. N. H. J. M.

Ammonium Iodide, its Solubilities and the Absence of a Transition Point. ALEXANDER SMITH and HERBERT E. EASTLACK (*J. Amer. Chem. Soc.*, 1916, **38**, 1500—1502).—Ammonium iodide crystallises in cubes, whilst the bromide and chloride form pentagonal icositetrahedra. Since it is probable that both these are transformed into cubic forms above their respective transition temperatures, there is some ground for the supposition that ammonium iodide will exist in two forms connected by a transition point.

Measurements of the solubility of ammonium iodide in water between $-19°$ and $136°$ afford no evidence of the existence of such a transition temperature. H. M. D.

The 'Spitting' of Silver. W. STAHL (*Metall und Erz.*, 1915, **12**, 501—504).—Crude silver containing iron sulphate is liable to 'spit' at the moment of solidifying. This effect has been attributed to sulphur dioxide. This gas is, however, insoluble in fused silver (Sieverts and Bergner, A., 1913, ii, 321). Silver is known to react with sulphur dioxide according to the equation $4Ag + 2SO_2 \rightleftarrows Ag_2SO_4 + Ag_2S$, or in presence of oxygen, $4Ag + 2SO_2 + 2O_2 \rightleftarrows 2Ag_2SO_4$. As the dissociation temperature of silver sulphate is 1030°, it can exist in contact with molten silver, and forms a slag on the surface. If more strongly heated, dissociation takes place: $Ag_2SO_4 = 2Ag + SO_2 + O_2$. The oxygen then dissolves in the silver, and is liberated on solidification, so causing the violent effect which has been observed. C. H. D.

Action of Hydrogen Sulphide on Mixtures of the Alkaline Earths with the Alkalis and with Oxides of the Heavy Metals. II. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1915—1916, **51**, 951—962. Compare this vol., ii, 324, 325).—The effect of strontium and lithium oxides on the action of hydrogen sulphide on sodium hydroxide or potassium hydroxide is considerably less energetic than that of calcium oxide or barium oxide, no incandescence being observed under the conditions used. The incandescence obtained with mixtures of sodium (or potassium) hydroxide and calcium (or barium) oxide cannot be attributed to the presence or formation of peroxides. The alkali peroxides (not, however, of recent preparation) act almost like the hydroxides, whilst barium, magnesium, and lead peroxides have no action. Mixtures of calcium

(or barium) oxide with mercuric or nickel oxide also react vigorously with hydrogen sulphide and, when the constituent oxides are in definite proportions, vivid incandescence or even explosion takes place. When incandescence occurs with mercuric oxide, sulphur dioxide is formed, and this reacts with the hydrogen sulphide, giving colloidal sulphur, which is precipitated by water in a special, blue form. No incandescence is observed when hydrogen sulphide acts on pumice and mercuric oxide, or on a mixture of calcium (or barium) oxide with ferric oxide, cuprous or cupric oxide, or litharge.

T. H. P.

Composition and Solubility of Calcium Hydrogen Carbonate. ALFREDO CAVAZZI (*Gazzetta*, 1916, **46**, ii, 122—135).—The author demonstrates the accuracy of the common supposition that the salt formed by the action of carbon dioxide on lime water or by that of a water more or less rich in carbon dioxide on the normal carbonate is calcium hydrogen carbonate of the composition $Ca(HCO_3)_2$. The maximum quantity of calcium carbonate which, after prolonged shaking (not less than ten hours), dissolves at 0° in 1 litre of water saturated with carbon dioxide and maintained so in presence of the gas at atmospheric pressure is 1·56 grams, that of calcium hydrogen carbonate being, therefore, 2·5272 grams. Under similar conditions and after shaking extending over some days, 1 litre of water at 15° dissolves 1·1752 grams of calcium carbonate, and consequently contains 1·9038 grams of calcium hydrogen carbonate. When a very violent current of carbon dioxide is passed into lime water saturated at 15° the latter becomes at first very turbid, but after about a minute almost clear and highly supersaturated with carbon dioxide; this solution, which only persists for a short time, contains 2·29 grams of calcium carbonate or 3·71 grams of calcium hydrogen carbonate per litre. T. H. P.

Action of Hydrogen Sulphide on Mercuric Iodide. GIAMBATTISTA FRANCESCHI (*Boll. chim. farm.*, 1916, **55**, 481—483). —Study of this reaction in alcoholic solution shows that it takes place in three phases, with formation of three different compounds, according to the conditions. These phases may be represented thus: (1) $H_2S + 2HgI_2 = 2HgI + 2HI + S$; (2) $6HgI + H_2S + 4S = 2(2HgS,HgI_2)$; and (3) $2HgS,HgI_2 + H_2S = 3HgS + 2HI$. Thus, the action of hydrogen sulphide on mercuric and mercurous salts always yields mercuric sulphide, the mercuric salts being previously reduced to mercurous salts, and an intermediate compound formed which may be regarded as a thiobasic mercury compound of the constitution $Hg(\cdot S \cdot HgR)_2$.

The *compound* $Hg(\cdot S \cdot HgI)_2$ forms a tobacco-coloured precipitate. T. H. P.

The Influence of Tungsten on Nickel. R. IRMANN (*Metall und Erz.*, 1915, **12**, 358—364).—Tungsten has very little tendency to dissolve in molten nickel at 1800°, but the alloys may be prepared by melting the nickel in an electric crucible furnace with carbon electrode, adding nickel oxide to remove carbon, then adding the

tungsten, and after all is melted, deoxidising by means of magnesium. A 50% alloy made in this way may be melted with excess of nickel in the electric furnace without difficulty.

For analysis, alloys containing less than 30% of tungsten may be dissolved in aqua regia with the addition of bromine; richer alloys are fused with potassium hydrogen sulphate.

Cooling curves are taken by melting 100 grams of each alloy in a carbon crucible lined with magnesia. The arrests are small, probably on account of the rapid rate of cooling. The freezing-point curve up to 50% W shows maxima at 1480° and 1495°, corresponding with the compositions $Ni_{16}W$ and Ni_6W respectively. The former is perhaps not a definite compound. Eutectic points are observed at 1426°, 1435°, and 1456°, at the compositions 2, 9·2, and 17 atomic % W respectively. Solid solutions are probably formed up to 2 atomic %.

The solubility of nickel in sulphuric acid, and its liability to corrosion, are greatly reduced by alloying with tungsten. The tensile strength shows a minimum at 15% W by weight, beyond which it increases rapidly. The alloy with 19% W may be rolled hot into thin sheets. C. H. D.

The Annealing of Nickel Brass (German Silver). F. C. THOMPSON (*J. Inst. Metals,* 1916, **15**, 230—263).—The specific volume of alloys containing 60% of copper and from 7 to 28% of nickel, the remainder being zinc, diminishes as the nickel content increases. At the same time the electrical resistance increases, and in the annealed state the specific resistance is independent of the copper-zinc ratio, and may be expressed by the formula $\sigma = 12 + Ni\%$ microhms per c.c. An abrupt change takes place in the resistance between 300° and 400°, the temperature being independent of the composition within the limits given. It is connected with the known instability of these alloys when used as resistance wires at a temperature above 300°, and may be due to a transformation of the compound $NiZn_3$. The heating and cooling curves, plotted by the inverse-rate method, do not exhibit any discontinuity, but it is well marked in the thermo-electric properties. When the hard-rolled alloys are annealed at different temperatures and tested for hardness by the Brinell method, a clear increase of hardness is found to take place at 300—330°. This temperature is slightly lowered by long annealing, but otherwise the influence of time is negligible. C. H. D.

Mineralogical Chemistry.

Composition of Selensulphur from Hawaii. GLENN V. BROWN (*Amer. J. Sci.*, 1916, [iv], **42**, 132—134).—A specimen of selensulphur collected at the crater of Kilauea by J. D. Dana in 1840 shows an orange-red to sulphur-yellow, crystalline encrustation on

slaggy lava. Deducting 83·72% of impurities, the analysis of this material indicates the presence of sulphur, 94·82%, and selenium, 5·18%, corresponding with the atomic ratio 45·5 : 1. Tellurium is absent. This material would therefore be more correctly described as a seleniferous sulphur, rather than as 'selensulphur.' L. J. S.

Artificial Mimetite (Lead Chlor-arsenate). C. C. McDONNELL and C. M. SMITH (*Amer. J. Sci.*, 1916, [iv], **42**, 139—145).—Lead monohydrogen arsenate ($PbHAsO_4$) is slightly soluble in a boiling solution of ammonium chloride, and when this solution is poured into a large volume of cold water a gelatinous precipitate with the composition of mimetite, $Pb_4(PbCl)(AsO_4)_3$, is formed. The same compound is obtained (slowly in the cold, but rapidly on warming) when the lead arsenate is digested with ammonium, sodium, or potassium chloride. The material so formed, when examined under the microscope, is seen to be mainly amorphous, but it contains a number of minute, hexagonal crystals. Larger crystals (up to 0·13 mm. in length) were obtained from a solution of the lead arsenate in hydrochloric acid, or by diluting a boiling saturated solution of sodium or potassium chloride to which arsenic acid and lead acetate had been added. The crystallised material has $D^{15} = 7·15$, and is apparently optically uniaxial with refractive indices, $\epsilon = 2·13$, $\omega = 2·16$ (the natural mineral being optically anomalous and biaxial). L. J. S.

Margarosanite, a New Lead-Calcium Silicate from Franklin, New Jersey. W. E. FORD and W. M. BRADLEY (*Amer. J. Sci.*, 1916, [iv], **42**, 159—162).—This new mineral was collected in the Parker shaft on North Mine Hill at the same time as the new species hancockite, nasonite, etc., described by Penfield and Warren in 1899 (A., 1900, ii, 88), where it occurred together with franklinits, willemite, etc. It is colourless and transparent, and forms lamellar masses with a perfect, pearly cleavage. The plates are bounded by two other good cleavages, forming an angle of 78°, which are nearly perpendicular to the lamellar cleavage. The optical characters indicate that the crystallisation is probably triclinic. Refractive indices, 1·730 and 1·795; D 3·991, H 2½—3. The mineral fuses with some difficulty in the oxidising flame, but readily in the reducing flame; it is decomposed by nitric acid with the separation of silica. The following mean of several analyses agrees with the metasilicate formula, $Pb(Ca,Mn)_2(SiO_3)_3$.

SiO_2.	PbO.	CaO.	MnO.	H_2O.	Total.
33·71	43·50	21·73	1·14	0·58	100·66

L. J. S.

Apatite from the Laacher See District. Sulphate-apatite and Carbonate-apatite. R. BRAUNS (*Jahrb. Min.*, 1916, *Beil.-Bd.* **41**, 60—92).—Small, colourless crystals of apatite occur in sanidinite and other ejected bombs of the Laacher See district, Rhine. In most instances these contain sulphate, and are therefore described as sulphate-apatite. These crystals give the axial ratio $a : c =$

1:0·73306, refractive indices $\omega_{Na}=1·6379$, $\epsilon_{Na}=1·6346$, and the following results on analysis:

	CaO.	$Fe_2O_3+Al_2O_3$.	MgO.	Na_2O+K_2O.	P_2O_5.	SO_3.
I.	54·70	0·70	—	n. d.	40·86	1·13
II.	53·60	1·10	0·14	2·70	39·66	1.30
III.	51·28	1·14	0·03	n. d.	37·97	1·35

	Cl.	F.	Insol.	Total less O for Cl & F.	Sp. gr.
I.	0·16	1·64	—	98·46	3·196—3·207
II.	0·42	0·93	0·60	99·97	3·200±0·01
III.	0·38	0·63	4·80	97·23	—

In each of these analyses there is an excess of lime over that required for the acids; the group CaO, as well as $CaSO_4$, therefore enters into the composition of apatite, the general formula of which is $3Ca_3P_2O_8,Ca[F_2,Cl_2,SO_4,CO_3,O,(OH)_2]$.

In another apatite, isolated from a cancrinite-syenite, the presence of a considerable amount of carbon dioxide suggests a carbonate-apatite, $3Ca_3P_2O_8,CaCO_3$. These crystals are said to differ from podolite (A., 1912, ii, 565) in having an optically *positive* biaxial shell surrounding an optically negative uniaxial nucleus. Incidentally in this connexion is mentioned the presence of carbon dioxide (CO_2 1·27%, together with Cl 1·08, and SO_3 7·97%) in noselite from the Laacher See, suggesting the presence of a carbonate-sodalite molecule. L. J. S.

Analytical Chemistry.

An Automatic Pipette. ALEXANDER LOWY (*J. Ind. Eng. Chem.*, 1916, **8**, 734—735).—A double-bored tap is placed on the upper stem of an ordinary pipette; one bore of the tap connects the upper stem with the bulb of the pipette, and the latter is filled in the usual way. The tap is then turned, and the pipette remains full. The second bore extends to the handle of the tap, and its outer end is closed with the finger; on giving the tap a half-turn and removing the finger, the contents of the pipette are discharged.

W. P. S.

Titrations with Oxalic Acid, Using Methyl-orange as Indicator. G. BRUHNS (*Zeitsch. anal. Chem.*, 1916, **55**, 321—340. Compare this vol., ii, 158).—Calcium, barium, strontium, and magnesium hydrogen carbonates may be titrated directly with oxalic acid solution, using methyl-orange as indicator. Alkali solutions, even when they contain carbonate or borate, may also be titrated with oxalic acid solution in the presence of methyl-orange provided that calcium chloride, strontium chloride, barium chloride,

zinc sulphate, cadmium sulphate, manganous sulphate, silver nitrate, or lead nitrate is also added. Ammonia solutions may be titrated similarly after the addition of calcium chloride or barium chloride. It is pointed out that the addition of 35 grams of crystallised boric acid per litre of $N/10$-ammonia solution renders the latter very stable; it may be kept for several days in an open flask without losing in strength. Attention is also drawn to the necessity of using water free from carbon dioxide in preparing the standard oxalic acid solution employed in the titrations. W. P. S.

Preparation of Diphenylamine-Sulphuric Acid Reagent. W. Tönius (*Zeitsch. Nahr. Genussm.*, 1916, **31**, 322).—This reagent may be prepared with ordinary sulphuric acid provided that the mixture is heated at 110° until any blue coloration due to the presence of nitric acid has disappeared. The heating expels the nitric acid and does not injure the reagent. W. P. S.

Estimation of the Water-Content of Substances. Artur Fornet (*Zeitsch. Nahr. Genussm.*, 1916, **31**, 329—332).—In the case of such substances as flour and meals, the water content can be estimated correctly only by heating the substance at 103° in a U-tube in a current of dry carbon dioxide or hydrogen, or by drying under reduced pressure over a dehydrating agent. The ordinary method of estimating moisture by heating the substance to constant weight in a water-oven is untrustworthy, for a substance so dried will undergo a further loss of weight if the temperature of the oven is raised. An empirical method for the estimation of moisture in flour is described, consisting in heating the substance on the pan of a lever-balance placed in an air-oven at 170°; the scale of the balance is so graduated that the percentage water content is indicated at the position where the pointer of the instrument remains constant. W. P. S.

Removal of Organically-combined Halogen by means of Catalytic Reduction. Estimation of Halogens. M. Busch and Hans Stöve (*Ber.*, 1916, **49**, 1063—1071).—It has been found that halogens can be split off from a large number of organic compounds by shaking an aqueous or alcoholic solution, rendered strongly alkaline, with palladinised calcium carbonate in an atmosphere of hydrogen, and details are now given of the application of this process to the estimation of halogens. Except in a few cases, the hydrogenation is complete in less than an hour, but the method has the serious disadvantage that the catalyst, although it may be prepared in bulk and kept for use as required, is easily "poisoned." For this reason, benzene, chloroform, acetone, and especially carbon disulphide, are useless as solvents, and compounds containing phosphorus, sulphur, or arsenic cannot be dealt with. Even the trace of phosphorus remaining in a sample of ethylidene dichloride which had been prepared with phosphorus pentachloride was sufficient to stop the influence of the catalyst.

Benzylidene chloride and benzotrichloride are completely de-

chlorinated by this method (compare Borsche and Heimbürger, A., 1915, i, 527), but dichloromethylmethylhexadienones are very resistant (compare Auwers and Lange, A., 1914, i, 50). J. C. W.

A Reagent for Detecting Free Chlorine in Town Drinking Waters. G. A. Le Roy (*Compt. rend.*, 1916, **163**, 226—228.)—The reagent is for use in detecting the presence of free chlorine in drinking waters purified by hypochlorites. The substance used is hexamethyltri-*p*-aminotriphenylmethane, and the reagent is prepared by dissolving 1 gram of the free base in 10 c.c. of cold hydrochloric acid, diluted with its own volume of water, and then making the solution up to 100 c.c. with distilled water. Formic acid may be used in place of hydrochloric acid, and the reagent can be kept for a long time in stoppered bottles. A few c.c. of this solution added to a litre of water gives an immediate violet coloration if free chlorine is present, and the reagent is sensitive to 3 parts of chlorine in 100,000,000 of water. The colour is intensified by the addition of a little sodium chloride to the water, and it is preferable to acidify the latter with formic or acetic acid. The reagent is not affected by traces of hydrogen peroxide, and is much less sensitive to the action of nitrites than is the starch-iodide reagent usually employed for detecting free chlorine. W. G.

Apparatus for Subliming and Weighing Small Quantities of Iodine. Gustave Fouque (*Bull. Soc. chim.*, 1916, [iv], **19**, 270—272).—A simple apparatus which consists essentially of two test-tubes about 15 mm. in diameter, the one fitting loosely inside the other. The outer tube is slightly constricted about 4 cm. from its base. The inner tube has a small hole in the side about 15 mm. from its base, so arranged as to be in the projecting portion when this tube is inserted mouth downwards into the other. The iodine to be purified is mixed with one-quarter of its weight of finely-ground potassium iodide and introduced into the outer tube, which is then placed inside a brass tube partly filled with sand to support the glass tubes in such a way that the constriction is a few millimetres inside the brass tube. An asbestos millboard shield is then fitted round the glass tubes down on to the top of the brass tube, and the iodine mixture is heated with a very small flame directed just below the constriction in the glass tube. The iodine slowly sublimes at the rate of about 1 gram per hour, and collects on the walls of the inner glass tube between the mouth and the opening in the side. When the sublimation is complete the inner glass tube is removed, placed inside another, into which it fits loosely, the whole is allowed to cool in a desiccator, and weighed. The two tubes having been previously weighed, the weight of iodine obtained is thus determined. The apparatus is sketched in the original paper. W. G.

Estimation of Small Quantities of Sulphide Sulphur. W. A. Drushel and C. M. Elston (*Amer. J. Sci.*, 1916, [iv], **42**, 155—158).—In the colorimetric method described, the depth of

colour of lead sulphide stains obtained from the sulphide sulphur of a known weight of substance is compared with a standard series of stains prepared from sulphide solutions of known sulphur content. The latter stains are obtained by boiling together definite quantities of sodium sulphide solution and hydrochloric acid in a flask and allowing the liberated hydrogen sulphide to escape through a long vertical tube, over the upper end of which is tied a piece of filter paper impregnated previously with lead acetate; the excess of lead is then washed out of the paper, and the latter is dried and labelled. A series of stains representing 0·0002—0·004% of sulphide sulphur is thus prepared. The actual estimation is made in a similar way. The tube over which the lead paper is tied may have a diameter of 18 mm. when dealing with relatively large quantities of sulphide sulphur, but a narrower tube should be used for quantities of less than 0·001%. The method may be employed for the estimation of sulphide sulphur in coke, gases, and paper.

W. P. S.

Volumetric Estimation of Thiosulphate in the Presence of Sulphite. A. SANDER (*Zeitsch. anal. Chem.* 1916, **55**, 340—342. Compare this vol., ii, 136).—Bodnár has described (A., 1914, ii, 67) a method for the estimation of thiosulphates which depends on the reaction of the latter with silver nitrate. The author finds that the method is simplified and rendered more rapid by the use of mercuric chloride in place of silver nitrate. When a mixture of sodium sulphite and thiosulphate is treated with mercuric chloride, the sulphite forms a soluble complex, $Na_2SO_3 + HgCl_2 = HgCl \cdot NaSO_3 + NaCl$, whilst the thiosulphate reacts according to the equations: $Na_2S_2O_3 + HgCl_2 = HgS_2O_3 + 2NaCl$;

$$HgS_2O_3 + H_2O = HgS + H_2SO_4;$$

and $2HgS + HgCl_2 = Hg_3S_2Cl_2$. The solution containing sulphite and thiosulphate is treated with an excess of mercuric chloride solution, a quantity of ammonium chloride is added to prevent the formation of mercuric oxide, and the mixture is titrated with $N/10$-sodium hydroxide solution, using methyl-orange as the indicator.

W. P. S.

Qualitative Separation and Detection of Tellurium and Arsenic and of Iron, Thallium, Zirconium, and Titanium. PHILIP E. BROWNING, G. S. SIMPSON, and LYMAN E. PORTER (*Amer. J. Sci.*, 1916, [iv], **42**, 106—108. Compare A., 1915, ii, 801).—Dilute hydrochloric acid, sodium sulphite, and potassium iodide are added to the solution containing tellurium and arsenic; tellurium is thus precipitated, and is separated by filtration. The filtrate is boiled to remove excess of sulphur dioxide, then treated with hydrogen peroxide, boiled to expel iodine, next rendered alkaline with sodium hydroxide, and treated with a further quantity of hydrogen peroxide to oxidise the arsenic. After the solution has been acidified to destroy sodium peroxide, it is rendered ammoniacal and the arsenate precipitated by the addition of magnesium chloride mixture. The filtrate from the arsenate may be tested for molyb-

denum by the addition of potassium thiocyanate and zinc in hydrochloric acid solution.

For the separation of iron, thallium, titanium, and zirconium the hydroxides are dissolved in sulphuric acid, and hydrogen peroxide is added; a red coloration indicates titanium. The solution is then rendered slightly alkaline with sodium hydroxide, sodium phosphate is added, and the mixture acidified with sulphuric acid containing hydrogen peroxide; the zirconium phosphate remains insoluble. After this precipitate has been separated, the solution is treated with sodium hydroxide, which precipitates the iron and thallium as hydroxides or phosphates; these are removed by filtration. The filtrate is acidified with sulphuric acid and treated with sodium sulphite and a small quantity of sodium phosphate, when the titanium is precipitated as phosphate. The precipitate containing the iron and thallium is dissolved in sulphuric acid, and the thallium precipitated as iodide by the addition of sodium sulphite and potassium iodide. The filtrate from the thallous iodide is boiled, treated with hydrogen peroxide, again boiled to expel iodine, and the iron identified by the thiocyanate test. W. P. S.

Estimation of Air, Water Vapour, and Nitrous Oxide in Mixtures of these three Constituents. G. A. BURRELL and G. W. JONES (*J. Ind. Eng. Chem.*, 1916, **8**, 735).—The following method of estimating air and water vapour in nitrous oxide (dentists' "laughing gas") is described. A sample of the gas is introduced into a tapped bulb-tube, provided with a manometer, and liquefied by immersing the tube in liquid air; the air is then withdrawn by a Töpler pump and its volume measured. The residual gas is next subjected to a temperature of $-78°$ (a mixture of solid carbon dioxide and acetone), and the nitrous oxide is withdrawn and measured. The frozen water remaining in the apparatus is allowed to melt and vaporise; its pressure is proportional to the amount of water-vapour present. Three samples of nitrous oxide examined each contained 2% of water-vapour and 2% of air. W. P. S.

Detection and Estimation of Nitrates and Nitrites in Meats, Sausages, etc. DESIDER ACÉL (*Zeitsch. Nahr. Genussm.*, 1916, **31**, 332—341).—A method described previously by the author and Liebermann (this vol., ii, 342) may be used for the detection and estimation of nitrates and nitrites in meat preparations. The presence of starch, sodium chloride, formaldehyde, boric acid, salicylic acid, sugar, vinegar, or juniper oil does not interfere with the reaction. Nitrites are produced during the burning of wood, but the quantity of nitrite thus introduced into smoked meats is too small to affect the results. Potassium nitrate in meat is reduced rapidly to nitrite; 50% of the quantity which may be present is reduced in four days when the meat is kept at 10°. W. P. S.

The Rapid Estimation, by Chemical Analysis, of the Potability of Waters. COMTE (*J. Pharm. Chim.*, 1916, [vii], **14**, 135—140).—As indications of pollution of water the author

relies on the values obtained for the estimation of chlorides, ammonia and oxygen absorption, and, as an indication of actual microbic life, on the amount of variation between the nitrite contents of a sample, when drawn and after a lapse of twenty-four hours. The results for the first three analyses should be compared with previous analyses of the same water, or the analyses of other waters from the same geological region. W. G.

Estimation of the Alkalinity of Waters. DHOMMÉE (*Ann. Chim. anal.*, 1916, **21**, 157—160; from *Bull. sci. pharmacol.*, 1916).—If the alkalinity of the water is due principally to calcium salts, 100 c.c. of the sample are treated with 6 drops of resazurine (0·1 gram of the substance dissolved in 500 c.c. of water containing 1 c.c. of $N/10$-ammonia) and titrated with $N/50$-sulphuric acid; 0·3 c.c. is subtracted from the quantity of acid used, this amount being required by the indicator. Waters containing chiefly magnesium salts are titrated similarly, but, in this case, 15 drops of a 0·2% lacmoid solution (in alcohol) are used as the indicator, and no correction is required. The results obtained by the use of the indicators mentioned are more trustworthy than those found when methyl-orange is employed. W. P. S.

Estimation of the Alkalinity and Phosphoric Acid Content of the Ash of Feeding Stuffs. I. M. KOLTHOFF (*Chem. Weekblad.*, 1916, **13**, 910—914).—A criticism of Farnsteiner's method for determining the alkalinity of the ash of foods.
A. J. W.

Estimation of Aluminium. C. F. SIDENER and EARL PETTIJOHN (*J. Ind. Eng. Chem.*, 1916, **8**, 714—716).—In the ordinary method of estimating alumina by precipitation with ammonia, the excess of ammonia used should be as small as possible; boiling for one minute precipitates the aluminium hydroxide completely, and continued boiling may cause a portion of the precipitate to redissolve. There is no need to wash the aluminium hydroxide free from chlorides before it is ignited (compare A., 1915, ii, 842); when the precipitate is large, it must be heated over a blast-flame for forty minutes to ensure its being reduced to a constant weight.
W. P. S.

The Analysis of Aluminium and its Alloys. W. H. WITHEY (*J. Inst. Metals*, 1916, **15**, 207—229).—It is desirable to avoid methods which involve separation of the aluminium, on account of the bulkiness of the precipitates. For alloys of aluminium and zinc, 1—2 grams are dissolved in dilute hydrochloric acid and diluted to 400 c.c. A 50% solution of sodium hydroxide (purified by alcohol) is now added, and when the precipitate has redissolved, 15—30 c.c. in excess are added. The solution is heated to boiling and the zinc precipitated by a rapid stream of hydrogen sulphide. The precipitate is collected, washed with boiling water containing sodium sulphide, and dissolved in hydrochloric acid.

Traces of aluminium are removed by precipitation with ammonia, the alumina being twice reprecipitated, and the zinc is then estimated as pyrophosphate.

For alloys containing less than 10% of copper, from 2 to 5 grams are dissolved in warm dilute hydrochloric acid (1 : 5). The greater part of the copper remains insoluble, and may be filtered off and dissolved in nitric acid. Hydrogen sulphide is passed through the filtrate, and the precipitated copper sulphide is added to the remainder. Should zinc be present, more hydrochloric acid must be added to prevent precipitation of zinc sulphide. The same method is recommended when manganese is present.

When the alloy contains magnesium, 2 grams are dissolved in a mixture of 30 c.c. of hydrochloric and 10 c.c. of nitric acids, and 15 c.c. of concentrated sulphuric acid are added after diluting somewhat. After evaporating to fuming and diluting, silicon and silica are removed and copper is precipitated as sulphide at 70°. The filtrate is boiled to remove hydrogen sulphide, and 15 grams of tartaric acid are added. After neutralising with ammonia, 5 grams of ammonium chloride are added, and hydrogen sulphide is passed at 70°. Iron, nickel, zinc, and some manganese are precipitated. The filtrate is acidified with acetic acid, boiled for some time, and sulphur and any nickel sulphide removed by filtration. The filtrate is concentrated to 300 c.c., cooled, and made alkaline with ammonia. A solution of 5 grams of sodium phosphate is now added, and after the precipitate has formed an excess of concentrated ammonia. It is advisable to reprecipitate, as the magnesium phosphate clings to the beaker. It may contain some silica and manganese, which may be estimated and allowed for. Manganese is best estimated in a separate quantity by a volumetric or colorimetric method.

Similar methods are used for the analysis of commercial aluminium. A satisfactory method of estimating carbon is not known. Silicon and silica should be estimated separately. Nitrogen is also present. C. H. D.

Standardisation with Ferric Oxide as the Basis of the Volumetric Estimation of Iron in Hydrochloric Acid Solution. L. Brandt (*Chem. Zeit.*, 1916, **40**, 605—607, 631—633).—The author's previously described method (A., 1908, ii, 899) for the preparation of ferric oxide to serve as an analytical standard gives a product which may contain traces of phosphoric acid and of platinum, and an additional precipitation as oxalate is therefore introduced into the process, which is now as follows: Iron, as free as possible from phosphorus and cobalt, is dissolved in hydrochloric acid, and after dilution and precipitation with hydrogen sulphide the filtrate is evaporated to a small volume, oxidised with nitric acid, evaporated to dryness with hydrochloric acid, dissolved in water, and extracted with ether, whereby an ethereal solution of ferric and ferrous chlorides is obtained. The ether is distilled off and the residue, dissolved in a little diluted hydrochloric acid, is completely reduced with sulphur dioxide with the addition of a

trace of iodine, and the clear ferrous chloride solution precipitated with an excess of ammonium oxalate. The ferrous oxalate, after thorough washing, is finally ignited in quartz glass vessels to constant weight. The ferric oxide thus obtained is perfectly pure, and gave results in complete agreement with those obtained, using 99·81% iron wire as standard. G. F. M.

Estimation of Chromium and Vanadium in Steel by Electrometric Titration. GEORGE LESLIE KELLEY and JAMES BRYANT CONANT (*J. Ind. Eng. Chem.*, 1916, **8**, 719—723).—In the absence of vanadium the following procedure is adopted for the estimation of chromium: One gram of the steel is dissolved in 60 c.c. of sulphuric acid (D 1·2), the solution oxidised with nitric acid, and evaporated until salts crystallise out; if carbides are not oxidised completely by this treatment, another portion of the sample should be dissolved in hydrochloric acid, oxidised with nitric acid, and evaporated with the addition of 60 c.c. of sulphuric acid. The solution is then heated to boiling, 10 c.c. of 0·26% silver nitrate solution and 5 grams of ammonium persulphate are added, the mixture boiled for ten minutes, treated with 5 c.c. of hydrochloric acid (1:3), and the boiling continued for a further five minutes. After cooling, a small quantity of sulphuric acid is added, and the chromium titrated electrometrically with ferrous sulphate solution (A., 1913, ii, 984). When vanadium is present, from 2 to 3 grams of the sample are dissolved in sulphuric acid (D 1·2), using 100 c.c. of this acid if necessary; the solution is diluted to 200 c.c., heated to 80°, treated with 5 grams of sodium phosphate, and titrated with $N/10$-permanganate solution until the first "grey" colour appears. The solution is then cooled to 10° by the addition of ice, sulphuric acid is added, and the mixture titrated electrometrically (this vol., ii, 274). The titrated solution is made up to a definite volume, a quantity corresponding with 1 gram of the steel is diluted to 300 c.c., and treated as described for the estimation of chromium, except that the solution must be cooled before the titration with ferrous sulphate solution. The amount of chromium present is calculated from the volume of ferrous sulphate solution used, as corrected for the quantity of vanadium present, and the quantity of chromium used in finding the end-point in this and the previous titration. W. P. S.

Separation of Vanadium from Phosphoric and Arsenic Acids and from Uranium. W. A. TURNER (*Amer. J. Sci.*, 1916, [iv], **42**, 109—110).—The "cupferron" method (this vol., ii, 347) is trustworthy for the separation of vanadium from phosphoric acid and arsenic acid provided that the precipitate is washed thoroughly. For the separation of vanadium from uranium, the "cupferron" precipitation has to be made from a strongly acid solution, since vanadium and uranium salts in neutral solution yield a precipitate of uranyl vanadate. About 10 c.c. of sulphuric acid should be present in each 100 c.c. of solution, and the precipitate is washed with 10% sulphuric acid containing 1·5 grams of "cup-

ferron" per litre. To ensure more complete separation, the washed precipitate is transferred to a beaker, dissolved in ammonia, then nearly neutralised, and cooled to 20°. After dilution, the solution is acidified, treated with a further small quantity of "cupferron," and the precipitate collected and washed. The uranium in the filtrate is precipitated by ammonia after the addition of ammonium chloride. The results obtained for uranium are trustworthy, but those for vanadium are slightly too high. W. P. S.

Detection of Methyl Alcohol by Rinck's Method. G. FENDLER (*Zeitsch. Nahr. Genussm.*, 1915, **30**, 228—230. Compare A., 1914, ii, 749).—This method was found to be untrustworthy, since ethyl alcohol yields formaldehyde under the conditions of the test. W. P. S.

Estimation of Glycerol in Wine by Rothenfusser's Method. LOUISE KALUSKY (*Zeitsch. Nahr. Genussm.*, 1915, **30**, 337. Compare A., 1912, ii, 607).—The calcium oxalate obtained in this method may be collected in a Gooch crucible containing a layer of asbestos which has been treated previously with hot dilute sulphuric acid and washed. The precipitate and asbestos are then transferred to a flask, the precipitate is dissolved in sulphuric acid, the solution filtered, and titrated as described. W. P. S.

Comparison of the Results Obtained by the Colorimetric and Gravimetric Estimations of Cholesterol. J. HOWARD MUELLER (*J. Biol. Chem.*, 1916, **25**, 549—560. Compare Bloor, this vol., ii, 275).—Pure cholesterol can be quantitatively estimated either by the colorimetric or the gravimetric (digitonin) method. When applied to blood, however, the colorimetric method gives results which are too high for true cholesterol, because they include other substances soluble in ether and chloroform which may or may not be related to cholesterol. The gravimetric estimation by means of digitonin appears to give accurate results. H. W. B.

Detection of Phytosterol and Cholesterol by means of Digitonin. OTTO PFEFFER (*Zeitsch. Nahr. Genussm.*, 1916, **31**, 38—40).—The precipitate obtained when the insoluble fatty acids of a fat or oil are treated with digitonin is most rapidly collected by pouring the heated mixture on a filter paper which is placed in a water-oven until the filtration is completed. Chloroform should not be added, as its presence retards the rate of filtration. The precipitate on the filter is then washed with hot chloroform and next with ether. After the ether has evaporated, the film of precipitate is easily removed from the filter, and is ready for treatment with acetic anhydride, etc. The author finds that hydrogenised fish oil, m. p. 52°, yields a cholesteryl acetate, m. p. 112°. W. P. S.

Estimation of Phytosterol by Precipitation with Digitonin. An Apparatus for Use in the Method. H. WAGNER (*Zeitsch. Nahr. Genussm.*, 1915, **30**, 265—270).—Of the various modifications proposed for this estimation the author prefers the procedure

described by Kuhn and Wewerinke (this vol., ii, 499). An apparatus for use in the method consists of a separating funnel in which the saponified fat is decomposed with acid and the liberated fatty acids are washed; a tap on the side of the funnel is provided for drawing off the ethereal solution of the fatty acids after the cholesterol and phytosterol have been precipitated with digitonin. The precipitate is then collected in a small filter tube which fits on to the lower end of the separating funnel; this filter is provided with a hot-water jacket. W. P. S.

Estimation of Phloroglucinol and Resorcinol by means of Furfuraldehyde. EMIL VOTOČEK and R. POTMĚŠIL (*Ber.*, 1916, **49**, 1185—1194).—The precipitates which phloroglucinol and resorcinol give with furfuraldehyde in hydrochloric acid solutions may be filtered, washed, and dried at 100—105°, and their weights used as a measure of these phenols. The constitution of the precipitate varies with the concentration of the acid and of the phenol, but the estimation is of practical value if the conditions are fulfilled (12% HCl; 100 c.c. for the volume, twenty-four hours for the time of precipitation, and a quantity of furfuraldehyde three times that of the phenol are recommended). The weight of the phenol is apparently obtained from a curve connecting the weights of the precipitate with those of pure specimens of the phenol as found by experiment. Phenol, quinol, toluquinol, and catechol do not give any appreciable precipitates, but the cresols, xylenols, pyrogallol, orcinol, and diresorcinol give heavy precipitates. Similarly, phloroglucinol- and resorcinol-carboxylic acids and certain tanning substances (from mimosa, maletto, and mangrove species) combine with the aldehyde.

As applications of the method, the estimation of phloroglucinol in phloretin, maclurin, and apigenin after hydrolysis, and of resorcinol in euxanthone are described. J. C. W.

Detection of Formic Acid in Vinegar. P. SZEBERÉNYI (*Zeitsch Nahr. Genussm.*, 1916, **31**, 16).—The test proposed depends on the fact that chromic acid is reduced by formic acid, but not by acetic acid. Twenty c.c. of the vinegar are mixed with 20 c.c. of concentrated sulphuric acid and to the hot mixture are added 3 c.c. of 50% chromic acid solution. If formic acid is present, carbon dioxide is evolved within a few minutes, and the mixture is coloured green owing to the reduction of the chromic acid. The test cannot be applied to wine vinegars or to vinegars containing a considerable quantity of extractives, since the latter, as well as the traces of alcohol in the wine vinegars, reduce chromic acid. W. P. S.

New Method of Extracting Lactic Acid [for its Estimation]. ERIK OHLSSON (*Skand. Arch. Physiol.*, 1916, **33**, 231—234).—In the estimation of lactic acid according to von Fürth-Charnass (A., 1910, ii, 807) as modified by Embden, the extraction with ether is a troublesome and lengthy process. For the isolation in a pure state the author finds ethyl acetate a better solvent, and when the

acid is merely to be estimated, amyl alcohol is much better. The liquid containing lactic acid is saturated with ammonium sulphate, filtered after twelve hours, and mixed with 1/10-volume of 50% sulphuric acid. It is then shaken with 2 volumes of amyl alcohol, which is then freed from the acid by shaking with sodium carbonate, and used similarly for four more successive extractions of the fluid. Traces of amyl alcohol are removed from the sodium carbonate extracts by three extractions with benzene, and the estimation is then carried out in the usual way. G. B.

The Estimation of the Strength of a Solution of Oxalic Acid. BLANCHETIÈRE (*Bull. Soc. chim.*, 1916, [iv], **19**, 300—308).—A comparative test of the various methods, both gravimetric and volumetric, shows that the most accurate method is the ordinary one of precipitation as calcium oxalate and weighing as carbonate. Of the volumetric methods, either titration of the hot solution with standard alkali or the iodometric method of Sander (compare A., 1914, ii, 482) may be used, the former being the more accurate. In using the iodometric method, it is preferable to employ a standard solution of sulphuric acid, rather than of picric acid, for determining the strength of the standard thiosulphate solution. W. G.

Untrustworthiness of Certain Methods for Determining the Forms of Combination of Organic Acids in Wine. W. J. BARAGIOLA and CH. GODET (*Zeitsch. Nahr. Genussm.*, 1916, **31**, 203—227).—Purely chemical methods for the estimation of free and combined volatile acids, tartaric acid, and lactic acid in wine do not give any correct indication of the actual state in which these acids exist in the wine. Whilst chemical analysis is necessary to indicate the kinds of acids present, the forms in which the latter occur are best ascertained by physico-chemical methods as proposed by Quartaroli and by Dutoit and Duboux. W. P. S.

Relation between the Most Important Physical and Chemical Constants of Oils and Fats. H. J. BACKER (*Chem. Weekblad*, 1916, **13**, 954—967).—For oils and fats composed solely of mixtures of glyceryl esters of saturated and unsaturated monocarboxylic acids, the relation between the refractive index (n), the density (d), the saponification value (V), and the iodine value (I) is given by the expression:

$$(n_t^2-1)/(n_t^2+2)\times 100/d_4^t = 33\cdot07 + 0\cdot00075I - 0\cdot01375V + 0\cdot002(t-15).$$

A. J. W.

Winkler's Bromine-Addition Method [for the Estimation of the Iodine Number of Fats and Oils]. W. ARNOLD (*Zeitsch. Nahr. Genussm.*, 1916, **31**, 382—387).—This method (A., 1914, ii, 753) was applied to a large number of various fats and oils and found to yield results which agreed with those yielded by Hübl's method, but were somewhat lower than those found by the Wys method. In the case of fats with low iodine numbers, one hour's contact with the reagent is sufficient, but with linseed oil,

poppyseed oil, etc., about eighteen hours' contact is required. The mixture of oil and reagent must be kept in the dark; if exposed to light, bromine is substituted as well as added, and the iodine number obtained is much too high. The potassium bromate and bromide may be dissolved in one solution; this keeps well and does not alter in strength. W. P. S.

Estimation of Acetone in Presence of Ethyl Alcohol. JITENDRANATH RAKSHIT (*Analyst*, 1916, **41**, 245—246).—Acetone is converted into iodoform in the presence of calcium hydroxide solution; the use of the latter in place of potassium hydroxide almost entirely prevents the formation of iodoform from ethyl alcohol. A portion of the sample, containing about 0·05 gram of acetone, is placed in a flask, 300 c.c. of calcium hydroxide solution are added, the flask is closed loosely with a rubber stopper, and its contents are heated at 35°; 5 c.c. of $N/5$-iodine solution are now added, drop by drop, the mixture is shaken for five minutes, another 5 c.c. of iodine solution are then added, and so on, until 40 c.c. of iodine solution have been added. If, during the addition of the iodine solution, the colour persists after thorough shaking, more calcium hydroxide solution must be added. Ten minutes after the final addition of iodine the mixture is cooled, starch solution and 15 c.c. of $N/1$-sulphuric acid are added, and the excess of iodine is titrated with $N/10$-thiosulphate solution. One c.c. of $N/5$-iodine solution is equivalent to 0·00193 gram of acetone. One c.c. of ethyl alcohol absorbs 0·8 c.c. of $N/5$-iodine solution. In mixtures containing 1 part of acetone and 10 parts of ethyl alcohol, the method yields trustworthy results; in the case of mixtures consisting of 1 part of acetone and 100 parts of ethyl alcohol, the results obtained are less trustworthy, since the correction for the ethyl alcohol is relatively large. W. P. S.

A General Reaction for Alkaloids containing a Phenolic Group of Vegetable or Animal Origin (Morphine and its Derivatives, Cupreine, Adrenaline, etc.). G. DENIGÈS (*Bull. Soc. chim.*, 1916, [iv], **19**, 308—311).—The reaction common to most phenols of giving a coloration with a solution of titanic anhydride in concentrated sulphuric or hydrochloric acid (compare Hauser and Lewite, A., 1912, i, 847) is applicable to those alkaloids of animal or vegetable origin which contain a phenolic group. The reagent is best prepared by leaving some rutile in contact with nearly boiling concentrated sulphuric acid for several hours, allowing the liquid to cool, and decanting off the clear solution. A few hundredths of a milligram of the alkaloid preparation with a few drops of this reagent will give the colour, which varies from blood-red with morphine to deep orange with hordenine. Proteins, containing a tyrosine group, also give an orange colour with the reagent. W. G.

General and Physical Chemistry.

Absorption Spectra and a Simple Method for Determining them. FRITZ WEIGERT (*Ber.*, 1916, **49**, 1496—1532).—An important discussion of the utility of the various methods for observing and recording absorption spectra. The need for making quantitative determinations, as, for example, by Bielecki and Henri's method (A., 1912, ii, 882), when basing discussions of chemical constitution on these spectra, is strongly emphasised, and a simple arrangement is described by which such estimations can be quickly made in the visible region. In principle, a standard substance of known absorption is chosen, and the wave-lengths are found at which the unknown substance has the same absorption. The standard substance must therefore fulfil very rigid requirements; it must obey Beer's and Lambert's laws, must be easily obtained in a constant degree of purity, and must be quite stable. A neutral grey substance would be best, for its "typical colour curve" (log . extinction plotted against wave-length) would be parallel to the abscissæ axis, but such a material is yet to be found. For the time being, a solution of equimolecular quantities of copper sulphate and potassium chromate in 2*N*-ammonia solution is recommended. Cells of equal width and evenly illuminated, containing the standard and the unknown solution, are placed before the slit of a spectroscope and viewed through a slit placed in the crossed-wires plane of the ocular, before which the spectrum can be moved by a wave-length drum or other graduated arrangement. The points at which the two solutions appear to be equally bright are then noted, observations in the dark red and blue being simplified by interposing red or blue screens. The measurements are then repeated for other dilutions, and the concentrations and wave-lengths are tabulated. From the extinction of the standard solution for a particular wave-length, the extinction of the unknown solution for the same wave-length can therefore be calculated and then its logarithm plotted in the usual way. J. C. W.

Relation between the Configuration and Rotation of Epimeric Monocarboxylic Sugar Acids. II. P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1916, **26**, 355—365. Compare this vol., ii, 3).—The sodium and brucine salts of several pairs of epimeric monocarboxylic sugar acids have been prepared and their specific rotations ascertained. From the results the rotations due to the *a*-carbon atoms have been calculated and found to be in agreement with the views expressed in the previous communication (*loc. cit.*). The following rotations, $[\alpha]_D^{20}$, are recorded: sodium gluconate, $+11{\cdot}78°$; brucine gluconate (m. p. 155°), $-15{\cdot}95°$; sodium mannonate, $-8{\cdot}82°$; brucine mannonate (m. p. 212°), $-25{\cdot}70°$; sodium gulonate, $+12{\cdot}68°$; brucine gulonate (m. p. 162—164°), $-19{\cdot}59°$; sodium idonate, $-2{\cdot}52°$; brucine idonate (m. p. 188°), $-25{\cdot}79°$;

sodium galactonate, +0 40°; brucine galactonate (m. p. 170°), −21·01°; brucine talonate (m. p. 132°), −26·15°; sodium allonate, +4·30°; brucine allonate (m. p. 160°), −21·28°; sodium altronate, −4·05°; brucine altronate (m. p. 158°), −23·82°; calcium chitonate, +33·65°; brucine chitonate (m. p. 222°), −8·47°; calcium chitarate, +70·29°; brucine chitarate (m. p. 195°), −2·96°.
H. W. B.

Optical Rotation of Epimeric α-Hexosamic Acids. P. A. LEVENE (*J. Biol. Chem.*, 1916, **26**, 367—372. Compare preceding abstract).—It has been shown (*loc. cit.*) that in each pair of hexonic acids the member which has the same configuration of the α-carbon atom as *d*-gluconic acid possesses either a higher dextrorotation or a lower lævorotation than the epimeride. It follows from this that in mixtures of unequal parts of two epimeric acids the one which possesses a higher dextro- or a lower lævo-rotation contains a higher proportion of the member having the configuration of the α-carbon atom as in dextrose. Further, having the value of the rotation of one epimeride in its pure form, and that of a mixture of the two, it is possible to draw a conclusion regarding the configuration of the α-carbon atom in each epimeride. On these grounds the author has compared the rotations of epimeric α-hexosamic acids with the view of finding an indication as to the respective positions of the amino-group in each member of a given pair.

The method is to heat the acid with pyridine in a sealed tube at 100—105° for periods varying from five to twenty-four hours, and to fractionate the resulting mixture of epimeric amino-acids until a fraction is obtained which differs markedly in rotatory power from the original substance.

The acids investigated were *d*-glucosamic, *d*-xylohexosamic, *d*-chondrosamic, and *d*-lyxohexosamic acids, and after the treatment with pyridine an increase in rotation occurred with each of the first three acids and a decrease with the last. Hence glucosamic acid has the configuration of mannosamic acid, xylohexosamic acid that of idosamic acid, chondrosamic acid that of talosamic acid, and lyxohexosamic acid that of galactosamic acid. H. W. B.

Rate of Loss of Activity of Illuminated Chlorine. MAX BODENSTEIN (*Zeitsch. Elektrochem.*, 1916, **22**, 293—294).—Polemical. An answer to Volmer's criticism (this vol., ii, 507) of the author's paper (this vol., ii, 463). J. F. S.

Photochemical Decomposition of Halogeno-acetic Acids in Benzene and Ether. HANS VON EULER (*Ber.*, 1916, **49**, 1366—1371. Compare A., 1913, ii, 939).—It has been shown that chloro- and bromo-acetic acids are decomposed in aqueous solutions in short-waved, ultra-violet light (just below 250 $\mu\mu$) into glycollic acid, the speed of the reaction being the greater in the case of the chloro-acid. It was thought to be probable that the acids undergo some preliminary "loosening" under the influence of light, which makes

them more open to attack by chemical agents, and, therefore, solutions in benzene and ether have been illuminated and then shaken for definite periods with sodium hydroxide in order to find whether more sodium chloride is formed than when an unilluminated solution is similarly treated. This is found to be so, but it is due to the fact that the halogens are already liberated in the solutions, and not that the acids have become more active. Fumaric acid and glycolide were found in the solutions after prolonged illumination. Strange to say, in these neutral solvents, bromoacetic acid is more unstable than chloroacetic acid. The decomposition is much greater in ether than in benzene. J. C. W.

Action of *X*-rays on Iodine and Starch Iodide in Aqueous Solution. H. BORDIER (*Compt. rend.*, 1916, **163**, 291—293. Compare this vol., i, 630).—*X*-Rays, like ordinary light, cause a decoloration of very dilute aqueous solutions of iodine or starch iodide, the only difference being that *X*-rays produce it in a few minutes, whereas the ultra-violet rays require several hours. The quantity of *X*-rays necessary varies with the proportion of iodine in the solution. W. G.

The Efficiency of Recoil of Radium-*D* from Radium-*C*. W. MAKOWER (*Phil. Mag.*, 1916, [vi], **32**, 226—229).—According to a mathematical investigation of Bohr, the efficiency of the recoil, *E*, of radium-*D* from a smooth plate on which radium-*A* has been deposited should be given by $1-a/2c$, where a is the "range" of the recoil-stream from radium-*A*, and c that of the recoil-stream from radium-*C*. This efficiency was determined by comparing the amount of polonium on the platinum surface on which the radium-*A* was initially deposited, and that on another surface to which radium-*D* had recoiled from the first, and found to be 0·687, which gives a value 0·626 for a/c for platinum. The value 0·72 can be deduced for gold from the experiments of Marsden and Richardson (A., 1913, ii, 91) for the ratio of the ranges of the corresponding α-particles producing the recoil, so that there appears to be a greater difference in the range of the recoil particles than in that of the α-particles. F. S.

The Product of the Radioactivity of Potassium and Rubidium. HILARY LACHS (*Chem. Zentr.*; from *Ber. Warschau. Wiss. Ges.*, 1915, 151—152; 1916, i, 872—873).—Since the products of the radioactive disintegration of potassium and rubidium must be calcium or strontium without appreciable change of the atomic weights, the atomic weights of calcium and strontium of as radioactive an origin as possible should show deviations from the accepted values in the direction indicated. Besides the common potassium and rubidium, isotopes having the atomic weights of calcium and strontium may exist. F. S.

Demonstration of the Ionisation Paths of the H-Particles which are Produced by Collision of α-Particles with Hydrogen Atoms. DEBENDRA BOSE (*Physikal. Zeitsch.*, 1916, **17**, 388—390).—By the use of Wilson's method, it has been found possible to

show the path of the H-particles which are expelled on collision of α-particles with hydrogen atoms. The photographic records show clearly the separation of the path of the α-particles into two distinct paths at the point of collision, corresponding respectively with the H-particles and the deflected α-particles. The observed number of the H-particles is in satisfactory agreement with that calculated from the Rutherford-Darwin formulæ. H. M. D.

Potential Changes on Illuminating Oxidising Agents. TORSTEN SWENSSON (*Zeitsch. physikal. Chem.*, 1916, **91**, 624—636). —The author has studied the influence of ultra-violet light on the oxidation potential of a solution of potassium dichromate and sulphuric acid. Solutions of potassium dichromate and sulphuric acid were placed in quartz vessels and the potential measured against a platinum electrode in the usual way. The solution was then subjected to the light from a mercury lamp, and the potential again measured after the light had been removed. The potential rapidly rises when the solution is illuminated, and on removing the light it slowly falls again. The same effects are observed whether the platinum electrode is present in the solution when it is illuminated or not. The cause of the large change in potential is in some way due to a mutual action of the dichromate and sulphuric acid, since both potassium dichromate solution and sulphuric acid when submitted alone to the action of the light only give a lowering of the potential, whereas chromic acid solution gives a slight increase. Experiments with N-, $N/2$-, and $N/3$-solutions show that the increase of potential is independent of the concentration. In the case of a solution of 1 mol. of potassium dichromate and 4 mols. of sulphuric acid per litre, the increase in the potential by illumination is 0·2280 volt. J. F. S.

Electrolytic Deposition of Brass. A. HÖNIG (*Zeitsch. Elektrochem.*, 1916, **22**, 286—293. Compare Spitzer, A., 1905, ii, 501, 611).—Experiments have been made on the deposition potentials of copper and zinc from alkaline cyanide solutions of these metals. The solutions used and the experimental conditions were similar to those employed by Spitzer (*loc. cit.*). It is shown that although the cathode in solutions which contain at least two molecules of potassium cyanide to one molecule of cuprous cyanide undergoes a strong polarisation during copper deposition, yet with small current densities this takes place in an almost reversible manner in solutions probably containing the salt $KCu(CN)_2$. If potassium cyanide is added gradually to a solution containing the salt $KCu(CN)_2$, the polarisation rapidly rises, even before the whole of the cuprous cyanide could have been converted into a salt, $K_2Cu(CN)_3$. The addition of $K_2Zn(CN)_4$ to a solution of $KCu(CN)_2$ brings about a strong polarisation of the copper deposition, whereby, as in the case of a solution of $K_2Cu(CN)_3$ and $K_2Zn(CN)_4$, the deposition potential of the copper is brought near to that of the zinc and electrolytic deposition of brass is rendered possible. The deposition potential of copper can be raised by keep-

ing or boiling the solution, and this change is supposed to be due to changes in small quantities of colloidal substances which are present. The action in these cases is held to be due to the production of mechanical passivity of the cathode. A large number of experiments have been made on the influence of the concentration of hydroxyl and cyanide ions on the colour of the brass deposited.

J. F. S.

Electrolytic Deposition of Nickel from Chloride Solutions. II. The Flaking of the Nickel. R. RIEDEL (*Zeitsch. Elektrochem.*, 1916, **22**, 281—286. Compare A., 1915, ii, 182).—In the electrodeposition of nickel on nickel cathodes from chloride solutions, it is found that the deposits are often spoiled by the flaking of the metal soon after the electrolysis has commenced. This difficulty may be obviated by effecting the separation at high temperatures. This process is not suitable for commercial work, and in consequence the experiments described in the paper were carried out with the object of procuring coherent deposits at ordinary temperatures. A number of substances were added to the electrolyte with the object of removing the possible causes cf flaking; these included glycerol and amyl alcohol, which affected the viscosity and surface tension respectively, wood extract, dextrin and other colloid substances, and potassium hypochlorite, nitrobenzene, titanium sulphate, acetylene, and turpentine, substances calculated to remove the hydrogen layer on the cathode. In no case was there any improvement of the deposit. It is shown that coherent deposits can be obtained on nickel cathodes at ordinary temperatures if the cathode is roughened, by either chemical or mechanical means, before use, and also if the cathode is coated with a thin deposit of nickel by any of the other known processes before use in the chloride solutions. The author tentatively suggests that the cause of flaking is to be found in the initial deposition of the metal in a labile form, which after a while changes to the stable form with increase of volume. J. F. S.

The Rectifying Action of Silicon and its Position in the Thermo-electric Series. FRANZ FISCHER and ERNST BAERWIND (*Physikal. Zeitsch.*, 1916, **17**, 373—376).—It has been shown previously that technical preparations of silicon show marked differences in their thermoelectric properties, some samples being positive and others negative with reference to gold. A similar difference is found when the rectifying action of silicon–gold combinations is examined. The combination of gold with thermoelectrically positive silicon conducts better when the current flows from silicon to gold, whilst in the case of thermoelectrically negative silicon larger currents are obtained when the current flows in the opposite direction. The rectifying action increases with increase in the strength of the current. The close correspondence between thermoelectric behaviour and rectifying action is also shown by heterogeneous samples of silicon, the thermoelectric properties of which vary according to the position of the metal content, the silicon being sometimes positive and at other times negative.

It is shown that the rectifying action has nothing to do with any polarisation due to the presence of moisture on the surface, and the authors draw the conclusion that there is a real connexion between the thermoelectric properties of silicon and its behaviour as a current rectifier. H. M. D.

The Electrocapillary Function. G. Gouy (*Ann. Physique*, 1916, [ix], **6**, 5—36).—A more detailed account of work already published (compare A., 1892, 553, 760; 1908, ii, 654). The apparatus employed is figured and described in detail. W. G.

The Conception of the Pressure of Expansion. L. Gay (*Ann. Physique*, 1916, [ix], **6**, 36—136).—A résumé of work already published (compare A., 1910, ii, 935, 1043; 1911, ii, 850, 1058; 1913, ii, 388, 668, 1027; 1914, ii, 108). W. G.

The Boiling Points of Homologous Compounds. H. C. Plummer (*Phil. Mag.*, 1916, [vi], **32**, 371—381).—The relations subsisting between the boiling points of homologous series of organic compounds are discussed, and certain formulæ connecting the boiling point with the number of carbon atoms in the homologous alkyl radicle are shown to afford a satisfactory representation of the observed boiling points.

Homologous series of alcohols, amines, aldehydes, cyanides, ketones, and nitro-compounds can be represented by a formula of the type $T=a(n+b)$, in which a and b are constants and n is the number of carbon atoms in the alkyl radicle.

The ethers of the series $C_sH_{2s+1}\cdot O\cdot C_rH_{2r+1}$, may be represented by the formula $T_{rs}=a+b(r+s)+c(r+s)^2+d(r-s)^2$, in which a, b, c, and d are constants. This formula is also applicable to the esters corresponding with $C_sH_{2s+1}\cdot CO\cdot O\cdot C_rH_{2r+1}$ and the acids of the series $C_nH_{2n+1}\cdot CO_2H$ may be represented by the formula $T=a+bn-cn^2$.

Halogen compounds of the series $C_nH_{2n+1}X$ may be represented by the formula $T=a\log(bn+c)$, in which a and b are independent of the nature of the halogen, whilst c varies with this, although its magnitude is related in a simple way to the atomic weight of the halogen.

Two formulæ are shown to afford satisfactory results for the normal paraffins C_nH_{2n+2}. The values given by $T=-69{\cdot}0+184{\cdot}65\sqrt{n}-6{\cdot}89n$ and $T=800\log(0{\cdot}2323n+1{\cdot}290)-70/2^n$ are in good agreement with experiment up to $n=19$. The latter formula is the more interesting in that it gives a satisfactory value for the boiling point of hydrogen, that is to say, for $n=0$, a result achieved by no other formula. H. M. D.

The Boiling Points and Critical Temperatures of Homologous Compounds. Sydney Young (*Sci. Proc. Roy. Dublin Soc.*, 1916, [ii], **15**, 93—98).—A review of the various formulæ which have been proposed for the calculation of the boiling point of the various members of the homologous series of normal paraffin hydrocarbons

(Walker, T., 1894, **65**, 193; Boggio-Lera, A., 1899, i, 843; Ramage, A., 1904, ii, 467; Ferguson, A., 1915, ii, 224), in which it is shown that none is so satisfactory as the author's formula, $\Delta=144{\cdot}86/(T^{0{\cdot}0148\sqrt{T}})$, where Δ represents the difference between the boiling point, T, of any normal paraffin and that of its next higher homologue, the greatest difference between the calculated and observed values for any member of the series CH_4 to $C_{19}H_{40}$ being 2·3. With the *iso*paraffins the agreement is less satisfactory.

It is shown that the author's statement that the ratio of the critical temperature to the boiling point is lower for normal compounds than for the isomeric *iso*-compounds is confirmed by the recently published data for the butanes (Burrell and Robertson, A., 1915, i, 933). D. F. T.

Transition of Sodium Sulphate. ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1916, **91**, 548—570).—A number of details and precautionary working points are given in connexion with the heatable pressure apparatus previously described (A., 1915, ii, 820). In the present paper preliminary details are given of experiments on the transition point of anhydrous sodium sulphate. It is shown that in addition to the well-known transition from thenardite (rhombic) to an hexagonal form, which is stated variously to occur at temperatures from 235—253°, a second transition occurs at about 400°. The author, by means of the pressure apparatus, finds that these two points lie at 240° and 385° respectively. A series of cooling and heating time curves tend to confirm the latter result, since a decided retardation in the rate of temperature change is observed at about 400°. In these heating and cooling experiments, an automatic photographic method of registering the temperature was employed. J. F. S.

A Comparison of the Relative Efficiency of Laboratory Reflux Condensers. M. V. DOVER and J. W. MARDEN (*J. Ind. Eng. Chem.*, 1916, **8**, 834—836).—The relative efficiency of various types of condensers was compared by boiling ethyl ether, chloroform, ethyl alcohol, etc., in a flask under the condenser arranged as a reflux, at such a rate that approximately equal weights were returned to the flask per second, and determining the weight of liquid lost at the end of specified periods of time. The bore of the condenser tube and the presence of constrictions were found to influence the efficiency, as any narrowing causes choking and a disproportionately large loss. The length is also a factor in the efficiency, especially in the Liebig type, where liquids of low boiling point are concerned, but with other forms the length of the jacket has less influence than is commonly supposed. Where a long condenser can be conveniently used, the Liebig is preferable, whilst the Friedrichs seems best in cases where a short condenser must be used. A short Liebig condenser can only be used to advantage when the rate of condensation is not greater than two to three drops per second, and the insertion of a plug of glass wool in the top is advisable to prevent the carrying away of the vapour by air currents. G. F. M.

The Applicability of Daniel Berthelot's Equation of State to the Behaviour of Vapours. HANS SCHIMANK (*Physikal. Zeitsch.*, 1916, **17**, 393—396).—From a comparison of the numbers obtained for the vapour density of various organic compounds by the use of the ideal gas equation and the equations of Berthelot and Nernst, it is found that results agreeing most closely with the experimental data are given by the Berthelot formula. In the case of hydrogen, however, Berthelot's formula is less satisfactory than the simple gas equation, whilst Nernst's empirical formula furnishes numbers in good accord with experiment.

A further comparison of the merits of the two formulæ has been made by combining them with the thermodynamic formula for the heat of vaporisation and comparing the heats of vaporisation calculated in this way with those obtained by experiment.

H. M. D.

Dispersion, Surface and Adsorption. CURT KÜHN (*Kolloid Zeitsch.*, 1916, **19**, 122—133).—The adsorption of brilliant-green from aqueous solution by certain mineral silicates has been examined with a view to ascertain the influence of the fineness of subdivision of the particles of the adsorbent on the quantity of dye adsorbed. Samples of the silicates of varying grades of fineness were obtained by shaking up the finely powdered mineral with water, allowing to settle for some time, and then syphoning off successive layers of the suspension. The results, interpreted in terms of the adsorption formula $x=\beta . c^p$, show that β increases with the degree of subdivision of the particles, but that p depends only on the chemical character of the adsorbent. In other words, the quantity of adsorbed substance depends, in a given case, on the magnitude of the surface of the adsorbent. H. M. D.

The Absorption of Colouring Matters by Charcoal and Silica. EDMUND KNECHT and EVA HIBBERT (*J. Soc. Dyers*, 1916, **32**, 226—230).—The absorption of crystal-scarlet, methylene-blue, and iodine by purified blood- and bone-charcoal has been examined, and from comparative experiments in which the nitrogen and oxygen content of the charcoal was varied by suitable chemical treatment, it was found that the absorptive capacity of the charcoal depends on the percentage of contained nitrogen and oxygen. The recorded data show that under certain conditions the increase or decrease in the amount of absorption is approximately proportional to the increase or decrease in the nitrogen content. The influence of the oxygen is shown most clearly in the absorption of methylene-blue.

Some few observations with silica as adsorbent in contact with solutions of methylene-blue indicate that the adsorption in this case is dependent on the capacity of the silica to absorb water. If hydration of the silica does not occur there is no absorption of methylene-blue. H. M. D.

Dissociation of Bromine Vapour. MAX BODENSTEIN and FRITZ CRAMER (*Zeitsch. Elektrochem.*, 1916, **22**, 327—339). —The degree of dissociation of bromine vapour into atoms

has been determined up to temperatures in the region of 1300° by measuring the pressure of a known weight of bromine vapour at a series of temperatures. The pressure measurements were made in a vessel of quartz glass by means of a quartz glass spiral manometer; temperature measurements were made by means of a platinum–platinorhodium thermo-element. The method employed was identical in most respects with that used by Bodenstein and Starck (A., 1911, ii, 20). A number of attempts to carry out the experiment in a platinum apparatus, with the object of reaching higher temperatures, failed, owing mainly to deformation of the apparatus under the pressure. It is shown that at the highest temperature employed, 1284°, and pressure, 721 mm., bromine is dissociated to the extent of 18·3%. The dependence of dissociation on temperature is shown to be in accord with the formula $\log K_p = -10100/T + 1{\cdot}75 \log T - 0{\cdot}0004090T + 4{\cdot}726 \times 10^{-8} . T^2 + 0{\cdot}548$. Calculations of the chemical constant from the determinations lead to the figure 1·88 for this quantity.

J. F. S.

Structure of the Capillary Layer. II. G. BAKKER (*Zeitsch. physikal. Chem.*, 1916, **91**, 571—592. Compare A., 1915, ii, 614). —A theoretical paper in which the nature of the capillary layer is further considered. It is shown that there is a third point in the labile portion of the gas–liquid isotherm which has the same thermodynamic potential as the points which represent the saturated vapour. This point, from its position, gives the specific volume and the pressure (in the long direction) in the capillary layer, and consequently also the energy and entropy per unit mass of the capillary layer. The author has chosen the two expressions $\epsilon = -A\rho + f(t)$ (Gauss, van der Waals) and $\epsilon = -A\sqrt[3]{\rho} + f(t)$ (Mills) as representing the two extreme forms of the energy of the homogeneous phase, and consequently of the capillary layer. Using these forms, it is found, for temperatures below the reduced temperature $\theta = 0{\cdot}9$, that the thickness of the capillary layer (ζ) is approximately 1—2 millimicrons. Since the surface tension is regarded as the amount of divergence from Pascal's law, the thickness of the capillary layer can be calculated by the formula $\xi = H/p_N - p_T$, in which H is the surface tension, p_N the vapour pressure, and p_T the pressure in the long direction of the capillary layer. Using this formula, it is found for carbon dioxide below $\theta = 0{\cdot}9$ that ζ = about 1·5 millimicrons. At temperatures above the reduced temperature $\theta = 0{\cdot}9$ it is shown that the thickness of the capillary layer increases rapidly with increase in temperature; thus for carbon dioxide the following values are found: 0°, $\theta = 0{\cdot}897$, $\zeta = 2{\cdot}03\ \mu\mu$; 10°, $\theta = 0{\cdot}920$, $\zeta = 2{\cdot}64\ \mu\mu$; 20°, $\theta = 0{\cdot}963$, $\zeta = 3{\cdot}88\ \mu\mu$; 28°, $\theta = 0{\cdot}989$, $\zeta = 7{\cdot}13\ \mu\mu$; 30°, $\theta = 0{\cdot}995$, $\zeta = 16{\cdot}52\ \mu\mu$, and 31·12°, $\theta = 0{\cdot}999$, $\zeta = 211\ \mu\mu$. The very small thickness of the capillary layer at temperatures below the reduced temperature $\theta = 0{\cdot}9$ is best seen from the number of molecular layers composing it; thus for benzene the following θ and N values are given: $\theta = 0{\cdot}493$, $N = 2{\cdot}8$; $\theta = 0{\cdot}629$, $N = 2{\cdot}7$; $\theta = 0{\cdot}753$, $N = 3$;

$\theta = 0.842$, $N = 3.7$; $\theta = 0.931$, $N = 4.5$; and $\theta = 0.976$, $N = 8.8$. In the case of carbon dioxide the following values are given: $\theta = 0.815$, $N = 3.8$; $\theta = 0.897$, $N = 4$; $\theta = 0.929$, $N = 5.3$; $\theta = 0.963$, $N = 7.4$; $\theta = 0.989$, $N = 13.77$; and $\theta = 0.999$, $N = 348$. From the fact that the capillary layer at low temperatures consists of only about three molecular layers, and in general of only a few molecular layers, except at the critical point, the author deduces that the sphere of action of the attractive force between the molecules cannot extend much beyond the adjacent molecule. The distance of the nearest molecule may be, however, about 10 molecular radii. From this it follows that the classical "agens" of the old theory of capillarity cannot maintain its original form, since it predicates a sphere of influence covering many molecules. It must, according to the present calculations, be regarded as a medium between the molecules, and between the atoms in the molecules, which plays the same rôle as the medium in the Faraday-Maxwell theory of electricity and magnetism. J. F. S.

Rhythmic Reactions. I. FRITZ KÖHLER (*Kolloid Zeitsch.*, 1916, **19**, 65—88).—When silver nitrate and ammonium dichromate react as a result of the diffusion which takes place when an aqueous solution of the one salt is placed in contact with a gelatinised solution of the other, precipitation rings are formed which exhibit rhythmic character. The phenomenon has been investigated in some detail.

When the ammonium salt is contained in the gelatin layer the ring formation varies with the concentration of the dichromate. At low concentrations the rings are only partly developed, and at high concentrations they are blurred, but over an intermediate range the ring system is well developed. If the gelatin layer contains the silver salt, similar results are obtained, except that no rings are formed when the concentration is small. The concentration of the gelatin also affects the ring formation in the sense that with increasing concentration the rings become less well defined.

The rate of development of the ring system has also been examined, and from these measurements conclusions are drawn relative to the nature of the diffusion processes. It seems probable that rhythmic precipitation phenomena in such gelatin–water systems are dependent on the existence of a more or less definite relation between the velocities of diffusion of the reacting substances and the velocity of crystallisation of the products of the reaction. H. M. D.

Molecular Condition of Water as Solvent. W. HERZ (*Zeitsch. Elektrochem.*, 1916, **22**, 349—351).—A theoretical paper in which it is shown, from calculations based on the Eötvös formula and the formulæ of Kistiakowsky (*J. pr. Chem.*, 1885, [ii], **31**, 177) and Trouton, that the molecular condition of water is changed by the act of solution. This change is small, but increases with increasing concentration. J. F. S.

Solutions. A. Reychler (*Chem. Zentr.*, 1916, i, 1004; from Pamphlet, Brussels, 1916, 32 pp.).—Reference is made to the affinity of water for the components of electrolytes to explain ion formation which proceeds in opposition to strong electrostatic forces. Around each ion a sphere of action is formed, the molecules of which are more or less restricted in movement. The surface of the liquid exerts a sort of repulsion on the molecules of the dissolved substance, since in their immediate neighbourhood the spheres of action cannot be completely formed. From this point of view the author deduces the laws of osmotic pressure and the lowering of the vapour pressure and of the freezing point. Of anomalous behaviour in electrolytes, the case, in particular, of such salts as lithium chloride is discussed. Here the molecular conductivity increases with dilution, but the osmotically determined molecular weight increases first of all with dilution, and then decreases again normally after attaining a certain maximum. This maximum is given, according to the author, at such a dilution that the spheres of action just touch one another, whence it is calculated that their diameter is four to six times that of the molecule, and that each ion is associated with about 165 mols. of water. In conclusion, qualitative experiments are described for the detection of the magnetic action of a current traversing an electrolyte. G. F. M.

Hydrotropic Phenomena. I. Carl Neuberg (*Biochem. Zeitsch.* 1916, **76**, 107—176).—Aqueous solutions of certain salts possess the power of dissolving certain substances which are not soluble in pure water. This phenomenon is designated hydrotropism. The salts of benzoic and salicylic acids, benzenesulphonic acid and many of its derivatives, naphthoic and various hydroaromatic acids, possess this property. The hydrotropic properties can be exerted on carbohydrates, alcohols, aldehydes, and many other classes of simpler compounds, as well as on alkaloids, proteins, fats, and lipoids. Many examples of the phenomenon are given in the paper. S. B. S.

Apparatus for Determining the Ions in a Solution. Ralph W. G. Wyckoff (*J. Amer. Chem. Soc.*, 1916, **38**, 1711—1712).—Simple apparatus has been devised for determining the ions into which a substance dissociates in solution. It consists of a U-tube with glass stop-cocks for closing the two arms, and a vertical tube which is fused into the middle part of the U-tube. The vertical tube (or jet-tube) terminates at the lower end in a fine aperture, and to the upper end is fused a thistle-tube carrying a stop-cock. The lower part of the U-tube has a ridge on each side of the jet-tube to prevent the liquid introduced from flowing in the lateral direction. Platinum electrodes are used. The apparatus is kept in a glass vessel through which cold water circulates. The tube is filled with the electrolyte, and the electrolysis is commenced. The substance to be tested is introduced, in a quantity of about 2 c.c., through the thistle funnel, and after half to one hour the arms of

the tube are closed and the contents tested. Examples of the use of the apparatus are quoted; thus, if nitric acid is used as electrolyte, it can be shown that after the addition of copper sulphate the Cu ion migrates to the cathode and the SO_4 ion to the anode compartment. It has also been employed for determining the charge on inorganic colloids. E. G.

An Electrolyte-Colloid-Crystalline Liquid. HÅKAN SANDQVIST (*Kolloid Zeitsch.*, 1916, **19**, 113—121).—A detailed investigation of the viscosity and optical properties of aqueous solutions of 10-bromophenanthrene-3(or 6)-sulphonic acid has shown that the colloido-chemical nature of the solutions varies in a very extraordinary way with the concentration. In dilute solution, the acid behaves like an ordinary electrolyte, but as the concentration increases the solutions become more and more colloidal in character, and ultimately a third stage is reached when the isotropic solution passes into a condition in which its behaviour resembles closely that of a crystalline liquid. Fall of temperature has the same effect as increase of concentration, and similar changes are brought about by the addition of certain foreign substances.

The viscosity of the isotropic colloidal solutions increases very rapidly with the concentration of the acid, and the temperature-coefficient of the viscosity is much greater than that of solutions of crystalloids. There appears to be no connexion between the viscosity and the electrical conductivity, for this remains approximately normal when the viscosity has become very large. Cryoscopic measurements indicate that the molecular weight of the acid is much greater in concentrated than in dilute solution. Foreign substances which produce the same effect as increase of the concentration and lowering of temperature are hydrochloric, nitric, and sulphuric acids. Weaker acids, such as acetic and monochloroacetic, have no appreciable influence, and sucrose is very much less active than the mineral acids.

In contrast with ordinary colloidal solutions, the properties of the bromophenanthrenesulphonic acid appear to be completely determined by the concentration, temperature, and foreign substances present in the solution and independent of the previous history of the solution. When the transition from the isotropic to the anisotropic condition takes place, there is no sudden change in the viscosity, and other properties and solutions of the substance under investigation afford, therefore, an example of a continuous change from a crystalloidal solution to a solution which shows the properties of an electrolyte, a colloid, and a crystalline liquid. The temperatures at which the isotropic colloidal solutions are transformed into crystalline liquids are sharply defined, and depend only on the concentration of the sulphonic acid and on the nature and quantity of the foreign substances present. H. M. D.

Protective Colloids. The Seed of Plantago Psyllium, L., as Protective Colloid. A. GUTBIER and J. HUBER (*Kolloid Zeitsch.*, 1916, **19**, 90—98. Compare this vol., ii, 231, 303).—The colloidal

solutions obtained by extracting the seeds of *Plantago Psyllium*, L., with water have been examined with special reference to the phenomena of ageing and the effects produced by the addition of electrolytes and the action of ultra-violet light. According to measurements of the viscosity, the extracts change fairly rapidly on keeping, but the stability is greatly increased by the addition of chloroform, toluene, trichloro-*tert*.-butyl alcohol, and ethyl acetate.

If a dilute solution of gold chloride is added to the extract and the mixture exposed to diffused daylight, stable solutions of colloidal gold are obtained without the addition of any reducing agent. H. M. D.

Imitation of Mucus Formation. MARTIN H. FISCHER and MARIAN O. HOOKER (*Kolloid. Zeitsch.*, 1916, **19**, 88—89).—The separation of mucous secretions from living cells cannot be attributed to diffusion because of the colloidal nature of the substances concerned. It is more probable that the mucins are secreted in non-hydrated form, and that this process is followed by hydration and swelling of the secreted colloid. To illustrate the process of colloid secretion, an experiment is described in which finely powdered acacia gum is triturated with cotton-seed oil. This is placed under the microscope and a drop of water allowed to come into contact with the oil layer. It is found that the surface of separation is in a state of motion, and that the particles of gum move towards the surface and are expelled into the aqueous layer, forming a mucous mass at the boundary. H. M. D.

Time Reaction of the Neutralisation of Carbonic Acid and the True Dissociation Constant of Carbonic Acid. LOTTE PUSCH (*Zeitsch. Elektrochem.*, 1916, **22**, 293).—An addendum to the author's paper (this vol., ii, 477), in which further details are given as to the method involved in arriving at the dissociation constant of carbonic acid. J. F. S.

Kinetics of Ether Formation. HANS VON HALBAN and WILHELMINE GAST (*Zeitsch. physikal. Chem.*, 1916, **91**, 593—604).—The kinetics of the formation of ethers in neutral or acid solution has been studied in several cases at temperatures of 65°, 45°, and 25°. Carefully measured quantities of benzyl bromide, allyl bromide, benzyl chloride, and ethyl bromide have been allowed to react with absolute ethyl alcohol at the above-mentioned temperatures, and the rate of reaction determined. A further series of experiments in which alcohol, containing known amounts of water, was used has also been carried out. In the case of absolute alcohol it is shown that the reaction is unimolecular and strongly influenced by temperature; thus in the case of allyl bromide the following values for k have been obtained: 65°, $k=2{\cdot}41\times10^{-4}$; 45°, $k=2{\cdot}93\times10^{-5}$; 25°, $k=2{\cdot}95\times10^{-6}$. The influence of water is greatly to accelerate the reaction; thus at 65° with benzyl bromide in absolute alcohol, $k=8{\cdot}6\times10^{-4}$, but in the presence of 3·75% of water $k=1{\cdot}8\times10^{-3}$,

and with 5·96% water $k=2·32\times10^{-3}$. Experiments were carried out with benzyl bromide and water and alcohol respectively in acetone solution, and from these it appears that the acceleration is not in reality due to an increase in the rate of ether formation, but rather to a secondary reaction between the water and the alkyl haloid. The experiments show that the formation of ethers is not the result of a reaction between the alkyl haloid and the alkyloxyl ion, but rather a reaction between the two undissociated molecules, at least in neutral and acid solutions. J. F. S.

Physico-chemical Experiments on the Additive Compounds of Thiocarbamides and Alkyl Iodides. HEINRICH GOLDSCHMIDT and ANTON HOUGEN (*Zeitsch. Elektrochem.*, 1916, **22**, 339—349. Compare A., 1913, ii, 284).—In an earlier paper (*loc. cit.*), Goldschmidt and Grini determined the rate of combination of alkyl iodides with various thiocarbamides. The present paper is a continuation of this work along several lines. The electrical conductivity in water solution has been determined at 25° for several dilutions, and the infinity value calculated by the Bredig method in the case of the following substances: thiocarbamide methiodide ($\lambda_\infty=118·4$), methylthiocarbamide methiodide ($\lambda_\infty=114·5$), ethylthiocarbamide methiodide ($\lambda_\infty=108·8$), ethylthiocarbamide ethiodide ($\lambda_\infty=104·3$), phenylthiocarbamide methiodide ($\lambda_\infty=106·6$), phenylthiocarbamide ethiodide ($\lambda_\infty=105·2$), *b*-phenyl-*a*-ethylthiocarbamide ethiodide ($\lambda_\infty=102$), *a*-phenyl-*b*-ethylthiocarbamide methiodide ($\lambda_\infty=103$), and *b*-phenyl-*aa*-diethylthiocarbamide methiodide ($\lambda_\infty=103$). A similar series of determinations were carried out in absolute alcohol solution at 25° with the substances: thiocarbamide methiodide ($\lambda=50·5$), allylthiocarbamide methiodide ($\lambda_\infty=49·7$), allylthiocarbamide ethiodide ($\lambda_\infty=47·6$), phenylthiocarbamide methiodide ($\lambda_\infty=49·6$), phenylthiocarbamide ethiodide ($\lambda_\infty=48·7$), *a*-phenyl-*b*-ethylthiocarbamide methiodide [$\lambda_\infty=49·1$ (mean)], *a*-phenyl-*b*-ethylthiocarbamide ethiodide ($\lambda_\infty=49·9$), *s*-diphenylthiocarbamide ethiodide ($\lambda_\infty=48·0$), *b*-phenyl-*aa*-diethylthiocarbamide methiodide ($\lambda_\infty=52·9$). These measurements indicate that the degree of ionisation of these substances depends to some extent on the number of substituting groups. The electrical conductivity of allylthiocarbamide ethiodide was also determined in alcohol containing respectively *N*- and 10*N*-water. The results show that the addition of water increases the degree of ionisation but reduces the infinity value. A large number of experiments have been carried out on the rate of addition of methyl iodide and ethyl iodide to various methyl-, ethyl-, allyl-, phenyl-, and piperidylthiocarbamides in solutions of methyl alcohol, ethyl alcohol, ethyl acetate, *iso*butyl alcohol, acetone, and nitrobenzene. The reactions were all carried out at 25°, and the amount of combination determined by two methods, the former of which depended on the electrical conductivity of the mixture and was previously employed by Goldschmidt and Grini (*loc. cit.*), and the latter consisted in removing a measured quantity of the reaction mixture, washing with ether to separate the unchanged components, and estimating

the amount of iodide in the resulting compound. The addition in every case is a second order reaction. Ethyl iodide is much slower in its action than methyl iodide, but the ratio of the velocities of the two iodides is not constant throughout the series of thiocarbamides. Mono-substituted thiocarbamides react more quickly than di- or tri-substituted thiocarbamides. The velocity of reaction is greatest in acetone and smallest in *iso*butyl alcohol, whilst the velocity is about the same in ethyl and methyl alcohols.

J. F. S.

Reactions of Ions and Molecules of Acids, Bases, and Salts. I. Reaction of Sodio-3-thio-1-phenylurazole and Ethyl Iodide in Absolute Ethyl Alcohol at 25°. J. CHANDLER and S. F. ACREE (*Zeitsch. physikal. Chem.*, 1916, **91**, 607—623).—The electrical conductivity and the degree of ionisation of solutions ($N/4$—$N/64$) of sodio-3-thio-1-phenylurazole in absolute alcohol have been determined at 25°. Using these values, together with the velocity data found for the reaction between sodio-3-thio-1-phenylurazole and ethyl iodide which have been determined for various concentrations, it is shown that both the ion and the undissociated urazole salt react with the ethyl iodide. The velocity constants are respectively $K(\text{ion}) = 0{\cdot}46$ and $K(\text{salt}) = 0{\cdot}17$. These results are in complete accord with the previously published results of Nirdlinger, Rogers, and Acree (A., 1913, ii, 205). Experiments were also made to determine the effect of the addition of salts on the velocity; these show that the neutral salt catalysis (NaI) is normal in the sense that the sodium iodide affects the ionisation of the sodio-urazole in accord with the Arrhenius theory of isohydric solutions.

J. F. S.

Studies in Catalysis. V. Quantitative Expressions for the Velocity, Temperature-coefficient, and Effect of the Catalyst from the Point of View of the Radiation Hypothesis. WILLIAM CUDMORE MCCULLAGH LEWIS (T., 1916, **109**, 796—815. Compare this vol., ii, 134, 135).—Further development of the idea that infrared radiation may be the active agent in promoting chemical changes of the ordinary or thermal type, including so-called uncatalysed as well as catalysed reactions in homogeneous systems, has led to the derivation of quantitative expressions for the velocity of such reactions and for the temperature-coefficients of the velocity.

In regard to the conditions which determine the reactivity of a substance, the radiation hypothesis leads to the conclusion that the active mass of a given molecular species is not simply proportional to its concentration, but to the product of the concentration and the density of the absorbable radiation present throughout the system. The radiation density is the amount of radiation, made up of quanta, corresponding with a certain frequency, ν, which is present in unit volume of the system when the radiation and the matter are in thermal equilibrium. The function of a positive catalyst is to increase the radiation density of that type which is absorbed by the reacting substance.

According to the quantum theory, the radiation density is determined by the frequency of the infra-red radiation, the temperature, and the refractive index of the system for radiation of the frequency in question. In passing through an absorption band, the refractive index undergoes a marked change in value, and for wave-lengths which are slightly greater than that corresponding with the band, the value of the refractive index is abnormally large. Since the radiation density is proportional to the cube of the refractive index, it follows that the number of quanta corresponding with the wave-length region just below the band are present in abnormally large amount throughout the system. The radiation density corresponding with the centre of the band is, however, not abnormally increased.

The radiation hypothesis suggests that the action of a positive catalyst consists in increasing the proportion of absorbable radiation, but even in the case of reactions in which catalytic effects are supposed to be absent, the interaction of two kinds of molecules may be attributed to the modification in the distribution of the infra-red radiation in such a way that more radiation is absorbed by one of these.

These views are applied in the discussion of the velocity of unimolecular reactions in gaseous systems in the absence and in the presence of a catalyst. The equation for the velocity in the former case leads to a relation which is identical with Einstein's statement of the law of photochemical equivalence, which is thus shown to be applicable to reactions caused by infra-red radiation. In presence of a solvent or other catalyst, factors come into operation which are not taken account of in the ordinary statement of Einstein's law.

The expressions obtained for the temperature-coefficients are all in agreement for small intervals of temperature with Arrhenius's empirical equation, which has been shown to be generally applicable. The magnitude of the temperature-coefficient depends on whether a catalyst is present or not, and it is further shown that any agency which increases the reaction velocity (positive catalyst) diminishes the temperature-coefficient, whilst any agency which diminishes the velocity (negative catalyst) increases the temperature-coefficient. This conclusion is shown to be in agreement with the available experimental observations. H. M. D.

Inorganic Chemistry.

Tautomerism of Nitrosylsulphuric (Nitrosulphonic) Acid. JOACHIM BIEHRINGER and WILHELM BORSUM (*Ber.*, 1916, **49**, 1402—1406).—In a discussion of the action of "nitrosylsulphuric acid" on organic compounds (A., 1915, i, 1060) it was shown that the acid behaves sometimes as the true nitrosylsulphuric acid,

$HO\cdot SO_2\cdot O\cdot NO$, and sometimes as nitrosulphonic acid, $HO\cdot SO_2\cdot NO_2$—in other words, that tautomeric forms exist in concentrated sulphuric acid solution. This being so, it should be possible to find a reaction in which it behaves in both ways simultaneously. It is now found that there is such a case. When a solution of dimethylaniline in concentrated sulphuric acid is slowly treated with the requisite sodium nitrite, both *p*-nitro- and *p*-nitrosodimethylaniline are formed. At 10—15° the yields are 8·33 and 71·45% respectively, whilst at 28—30° they are 42·85 and 39·33%, which suggests that the nitro-form of the acid is favoured at higher temperatures. J. C. W.

Oxidation Products of Various Graphites. A. LANG (*Chem. Zentr.*, 1916, i, 826; from *Montan. Rundschau*, 1916, **19**, 1—3).—The use of molten alkali for the purification of graphite is liable to cause changes in its constitution, and hydrochloric and hydrofluoric acids, etc., are to be preferred for the purpose. Oxidation of graphite by means of permanganic acid gives graphitic acids of variable composition, and more uniform results are obtained with a mixture of concentrated sulphuric and nitric acids and potassium chlorate. There are two graphitic acids occurring in leaflets, distinguishable from one another in colour and composition. The graphitic acids from Acheson, Ceylon, and Russian blast-furnace graphite are yellow, whilst those from Siberian, Italian, Corean, and cast-iron graphite are green, the former being richer in carbon and poorer in oxygen than the latter. Luzi's division of graphites into intumescent and non-intumescent varieties can scarcely be maintained, since the artificial, non-intumescent graphites gave graphitic acids of approximately the same composition as the intumescent natural variety. Cast-iron graphite forms an exception, as it approximates in its behaviour to the natural non-intumescent varieties. The colour of the graphitic acids diminishes in intensity in the light. Prolonged washing transforms them into a colloidal modification, whilst on further oxidation or long-continued heating at 120—130° they assume a darker, earthy-brown colour. In both cases disintegrative oxidation occurs. G. F. M.

The Productivity of the Extraction of Coal by Benzene. FRANZ FISCHER and WILHELM GLUUD (*Ber.*, 1916, **49**, 1460—1468).—The authors have extracted some representative coals with benzene in a special bomb apparatus, the solvent being gradually raised to about 275°, which implies a pressure of 55 atmospheres. They find that hard coal is not decomposed at this temperature (compare Wheeler, T., 1914, **104**, 130), and that, even after five such extractions, it is not much altered in appearance, although as much as 6·6% is dissolved. The yield of extracted substances is therefore higher than can be obtained by distillation, and it is remarkable that about half of the material is solid. Brown coal decomposes, giving volatile sulphur compounds, and 25% dissolves after three extractions. Although so rich in bituminous substances, cannel coal only dissolves to the extent of 4%

by the above treatment, or 1% at 80°. Apparently 275° does not represent a sufficiently high working temperature, for naphthalene at 350° extracts 25—30%, considerable decomposition also taking place. J. C. W.

Extraction of Coal by Liquid Sulphur Dioxide. FRANZ FISCHER and WILHELM GLUUD (*Ber.*, 1916, **49**, 1469—1471).—Exceptions might be taken to the use of an organic solvent at high temperatures in the extraction of coal for the purpose of studying its true ingredients, and search has therefore been made for an inorganic solvent which could be applied at low temperatures. Liquid sulphur dioxide is found to be more or less suitable, but the manipulative difficulties have not yet been overcome. Compared with benzene, however, it appears that this solvent gives an extract which is much poorer in solids, and it also has the effect of causing the coal to fall to a powder. Anthracite and cannel coal are scarcely attacked, but most hard coals behave in the above way. Brown coal gives an extract which is a typical resin, whereas the residue from a benzene extraction is a resin mixed with a true wax. J. C. W.

Transformation of Coal into Soluble Substances by means of Ozone. FRANZ FISCHER (*Ber.*, 1916, **49**, 1472—1474).—If powdered coal is suspended in water and submitted to a stream of ozone it gradually disappears, leaving a dark brown solution of a caramel-like substance with a strongly acid reaction. In one case 9·6 grams of coal dwindled to 0·7 gram, and 9·2 grams of substance were found in the solution. The investigation of the soluble matter, probably consisting of an acid or acids formed by the action of water on ozonides, is being pursued. J. C. W.

Singular Properties of Soda Lime. IV. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1916, **51**, 1094—1113. Compare this vol., ii, 324).—The efficiency of soda lime as an absorbent of vapours readily emitted under ordinary conditions from liquid and solid compounds, especially those exerting a toxic action on the animal organism, has been investigated. The results obtained are briefly as follows.

Chromium oxychloride: rapidly absorbed, no acid vapour passing. Thionyl chloride: immediately decomposed with development of much heat but no incandescence, no trace being allowed to pass. Ethyl chloroformate: absorbed with avidity, heat being developed; only faint alcohol–ethereal odour passes: $Cl{\cdot}CO_2Et + Ca{<}^{O}_{NaOH} =$ $NaCl + Et{\cdot}OH + CaCO_3$. Chloroacetone: absorbed with generation of heat and replacement of the irritant vapour by one with a pleasant odour: $CH_2Cl{\cdot}COMe + Ca{<}^{O}_{NaOH} = OH{\cdot}CH_2{\cdot}COMe +$ $NaCl + CaO$. ω-Bromoacetophenone: absorbed. Ethyl bromoacetate: not fixed. Ethyl α-chloroacetoacetate: readily absorbed.

Bromoacetyl bromide: immediately absorbed with liberation of heat. Benzyl bromide and chloride: absorbed. Chlorobenzene: not readily absorbed. Crude xylyl or xylylene bromide, probably a mixture of ω-bromoxylenes and ωω′-dibromoxylenes: readily absorbed. Acraldehyde: readily absorbed. Furfuraldehyde: rapidly absorbed with development of heat. Formaldehyde: absorbed. Thioformaldehyde: completely and rapidly fixed. Acetaldehyde: absorbed with development of heat. Pyrrole: not, or but slightly, absorbed. Indole and skatole: absorbed. Sulphur chloride: immediately absorbed with heating. Ethyl mercaptan: rapidly absorbed with marked development of heat. Thiophen: fixed either not at all or only in traces. Hydrocyanic acid: rapidly absorbed with moderate heating. Sulphur trioxide: inefficiently fixed. Acetic anhydride: rapidly absorbed. Various esters undergo hydrolysis. Gases and vapours of putrefaction: absorbed. Products of incomplete combustion of paper, wood, etc.: rendered quite odourless.

In presence of soda lime various synthetic reactions take place at the ordinary temperature; the results obtained in this direction are to be published later. T. H. P.

Separation of Cæsium and Rubidium by the Fractional Crystallisation of the Aluminium and Iron Alums, and its Application to the Extraction of these Elements from their Mineral Sources. PHILIP E. BROWNING and S. R. SPENCER (*Amer. J. Sci.*, 1916, **42**, 279—281).—The difference in solubility of cæsium and rubidium alums (100 parts of water at 15—17° dissolve 0·62 part of cæsium alum and 2·3 parts of rubidium alum) affords a means of separating the two elements. To obtain cæsium and rubidium from lepidolite, the mineral is decomposed by heating with calcium fluoride and sulphuric acid, the resulting solution freed from calcium sulphate, and then evaporated until the mixed alums crystallise; the crystals are separated, recrystallised, the liquor is added to the mother liquor from the first crop of crystals, and this mixed liquor concentrated to crystallisation, and so on. After thirteen recrystallisations, the crystals first formed yield pure cæsium alum, but about twenty-eight fractions have to be obtained before the rubidium alum is obtained in a pure state. If the mixed alums are dissolved in water, treated with ammonia, the aluminium hydroxide separated, the solution then evaporated and treated with ammonium ferric alum, the crystals which first separate consist of cæsium alum and are free from rubidium. Cæsium may be extracted from pollucite by decomposing the mineral with hydrochloric acid, separating the silica, and warming the acid solution with the addition of ammonium aluminium alum; on cooling, cæsium alum separates out. The crystals are twice recrystallised to obtain the pure alum; the remainder of the cæsium is obtained by a few crystallisations of the mother liquors. W. P. S.

Action of Ammonium Nitrate on Potassium Chlorate. R. SALVADORI (*Ann. Chim. Applicata*, 1916, **6**, 115—118).—The

author has studied the reaction between potassium chlorate and ammonium nitrate by means of the tensimeter, the curve obtained being compared with those representing the decomposition of each component of the mixture taken alone. The results obtained confirm the conclusion previously drawn (A., 1906, ii, 900). The potassium chlorate curve exhibits two transformation points, the formation of perchlorate taking place between 270° and 310°, and its subsequent decomposition at 400°. Between 180° and 240° ammonium nitrate melts and sublimes, and at the latter temperature decomposition proceeds with some rapidity. Ammonium chlorate begins to melt immediately above 60°, and at 90° the decomposition is explosive in character. The ammonium nitrate–potassium chlorate mixture has no true melting point, but decomposition into volatile products commences at 120°, that is, much nearer to the transformation point of ammonium chlorate than to those of the constituents of the mixture. The velocity of transformation is analogous to that of ammonium nitrate, and the curve of decomposition of the mixture may be regarded as parallel to that of ammonium nitrate. Above 220° the potassium nitrate phase begins, with melting point beyond 340°.

Calorimetric measurements show that $KClO_3 + NH_4NO_3 = KNO_3 + NH_4ClO_3 + 44,000$ cal., whilst, if the ammonium chlorate formed undergoes decomposition, the heat generated by the above reaction is increased to 125,000 cal. The decomposition of ammonium chlorate at 90° takes place according to the equation $NH_4ClO_3 = NOCl + 2H_2O$, the secondary reaction, $NOCl + H_2O = HNO_2 + HCl$, or, at higher temperatures, $2NOCl + H_2O = 2HCl + NO + NO_2$ also occurring. T. H. P.

Solubility of Mineral Phosphates. A. Aita (*Ann. Chim. Applicata*, 1916, **6**, 28—44).—Experiments have been made on the solubility of the phosphoric acid of natural phosphorites in 2% citric acid solution under different conditions. The initial rate of dissolution is diminished by the presence of calcium carbonate, but as the latter is gradually attacked by the citric acid and removed, the rate of dissolution of the phosphoric acid increases. Calcium salts in general produce a diminution in the solubility, but ammonium, alkali, and magnesium salts cause an increase, which varies with the concentration of the added salt and with the friability, fineness, and lime- or chalk-content of the phosphorite. The increase in solubility produced by these salts also varies in extent with the anion of the salt. These results are discussed in relation to the effect of the added salts on the equilibrium, $Ca_3(PO_4)_2 + 2C_6H_8O_7 \rightleftharpoons 2H_3PO_4 + Ca_3(C_6H_5O_7)_2$, and the conclusion is drawn that only salts of energetic acids with cations capable of giving rise to a soluble phosphate facilitate the dissolution of tricalcium phosphate; salts with anions weaker than that of citric acid exercise a negative action, the anions being displaced by that of citric acid. The author regards the solubility of basic phosphates of the Wiborgh type in citric acid as due to the presence, not of tetracalcium alkali phosphate, but of alkali salts.

According to these views, suitable mixtures of phosphorites with magnesium, alkali, or ammonium salts should find economical application in agriculture. T. H. P.

Causes Influencing the Solubility in Citric Acid of Difficultly Soluble Phosphates. A. AITA (*Ann. Chim. Applicata*, 1916, **6**, 119—131. Compare preceding abstract).—Further experiments show that free lime lowers the solubility of phosphoric acid in citric acid, because part of the latter is neutralised; the other constituents of natural phosphates, etc., also dissolve more readily when their free lime is eliminated. The secondary constituents of dephosphorisation slags may be divided into those which hinder the dissolution of the phosphoric acid, namely, lime, silicates, manganese, etc., and those which facilitate such dissolution, namely, sulphates, aluminium, and iron. Sulphates are present in these slags in only small proportions, but the effect of the iron and aluminium present more than counterbalances that of the lime, silicates, manganese, etc. The varying solubilities exhibited by these slags depend also to some extent on the varying solubility of the iron and aluminium present in citric acid. Like the mineral phosphates or phosphorites, basic slag contains its phosphoric acid as tricalcium phosphate, and the difference in price usual between the phosphoric acid in the two cases does not seem justified. Against Wagner's method of establishing the fertilising value of slags the criticism is advanced that it does not make proper allowance for the influence of the secondary constituents of the slag on the solubility of the phosphoric acid. T. H. P.

Reduction of Barium Sulphate to Sulphide. ARTHUR E. WELLS (*J. Ind. Eng. Chem.*, 1916, **8**, 770—777).—Experiments were made on the reduction of barium sulphate by means of carbon and also of reducing gases at varying temperatures from 650° to 1150°. The maximum reduction to water-soluble barium sulphide, 96—97%, was obtained at temperatures above 1000°, and when the operation was effected in an indirectly fired furnace, for example, in a muffle furnace, the use of 15—16% of carbon gave the highest fuel efficiency consistent with completeness of reduction of the sulphate. In reductions carried out in a directly fired furnace (cement kiln, a multiple hearth furnace, or a shaft furnace where hydrogen, hydrocarbons, or the products of combustion of the fuel were brought into contact with the sulphate) a larger proportion of barium compounds, insoluble in water, were formed, so that although the acid-soluble barium compounds in the best products formed 90—95% of the total, of these not more than 85—87% was water-soluble sulphide. In general, a rapid reduction at a high temperature produced less of these water-insoluble barium oxides and carbonates than a prolonged reduction at lower temperatures. Below 750° reduction by carbon or reducing gases was too slow to be of technical importance. G. F. M.

Precipitation of Magnesium Salts by Ammonium Carbonate. FR. FICHTER and RENÉ OSTERWALDER (*Zeitsch. anal. Chem.*, 1916, **55**, 389—392).—Ordinary ammonium carbonate in solution reacts essentially as a mixture of ammonium carbonate and ammonium hydrogen carbonate; if this solution is added to magnesium sulphate solution, crystalline hydrated magnesium carbonate, $MgCO_3,3H_2O$, is precipitated gradually. The precipitation is more rapid when the mixture is warmed. The crystals of the hydrated carbonate appear within thirty minutes when magnesium sulphate solution is mixed with ammonium carbonate solution to which ammonia has been added previously in such quantity that the proportion of ammonia to carbon dioxide corresponds with the formula $(NH_4)_2CO_3$; if this mixture is heated at 40°, an amorphous precipitate of basic magnesium carbonate (*magnesia alba*) is formed, which changes into the hydrated carbonate as the mixture cools. On treating magnesium sulphate solution with ammonium carbonate solution containing a greater proportion of ammonia than corresponds with the formula $(NH_4)_2CO_3$, basic magnesium carbonate forms in the cold, and changes in a few hours into the hydrated carbonate; if, however, the precipitation is made from a hot solution, the basic carbonate remains as such when the mixture cools. A double carbonate, $(NH_4)_2CO_3,MgCO_3,4H_2O$, is obtained by mixing, in cold solution, 1 equivalent of magnesium sulphate with 10 equivalents of ammonium carbonate, of the composition $(NH_4)_2CO_3$. W. P. S.

Density of Radio-lead from Pure Norwegian Cleveite T. W. RICHARDS and C. WADSWORTH, 3d (*J. Amer. Chem. Soc.*, 1916, **38**, 1658—1660).—A specimen of carefully selected Norwegian cleveite was converted into the nitrate, and the latter purified by fractional crystallisation. From the purified nitrate the chloride was precipitated with hydrochloric acid, and further purified by repeated recrystallisation. The density of pure radio-lead, prepared from the chloride, was determined at 19·94° by the method adopted in the case of Australian radio-lead (this vol., ii, 251), and found to be 11·273 as compared with 11·289 for the Australian radio-lead and 11·337 for ordinary lead. The decrease in density is almost exactly proportional to the decrease of the atomic weight in these samples, the atomic weight of the Australian radio-lead being 206·35 and that of the Norwegian lead 206·085. The atomic volume of the latter, 18·281, is practically equal to the value 18·277 found for ordinary lead and to the value 18·279 found for the Australian radio-lead. E. G.

The Solubility of Leucite in Sulphurous Acid. J. SCHROEDER (*J. Ind. Eng. Chem.*, 1916, **8**, 779—780).—Sulphurous acid exerts a selective solvent action on the potassium contained in leucite, a metasilicate of aluminium and potassium, $K_2O,Al_2O_3,4SiO_2$, occurring in large quantities in the Leucite Hills in Wyoming, U.S.A. Thus a sample of leucite rock containing 9% K_2O, on treatment in fine powder with a solution of sulphur dioxide, gave up about

75% of its potassium content against 25—26% of total matter dissolved. A method for the extraction of potassium salts and the utilisation of waste sulphurous fumes is thereby indicated.

G. F. M.

Passivity of Iron. A. SMITS (*J. Soc. Chem. Ind.*, 1916, **35**, 928; from *De Ingenieur*, 1915, 357—359).—A theory of the passivity of iron is developed, based on the assumption that, in addition to uncharged atoms and free electrons, the metal contains two different kinds of ions of different valency, viz., α ("base") ions, and β ("noble") ions. These two kinds of ions are in equilibrium, and the production of the passive state is to be ascribed to the destruction of this equilibrium. In the anodic solution of a metal, polarisation occurs because the metal tends to dissolve more rapidly than the equilibrium can be established, so that a concentration of β-ions takes place at the surface. Ordinary iron always contains hydrogen, and hydrogen ions, like halogen ions, greatly accelerate the change from the passive to the active state. In the anodic solution of iron, the concentration of hydrogen in the iron falls, owing to solution, and consequently its accelerating influence on the establishment of equilibrium between the two kinds of ions decreases until, by increasing the current density so that the potential rises to the value corresponding with the anodic evolution of oxygen, the hydrogen is completely removed from the surface of the iron and a maximum disturbance of the equilibrium (production of the passive state) is attained. This condition persists for a short time after the breaking of the circuit, but hydrogen soon diffuses from the interior of the metal and catalytically accelerates the establishment of equilibrium, and hence the active state. When iron is immersed in strong nitric acid, the α-ions dissolve with great rapidity, and hydrogen ions are also removed from the surface of the metal, so that the passive condition is established. In ferrous chloride solution, on the other hand, passivity is not produced, because both the chlorine ions and the hydrogen ions catalytically accelerate the change from the passive to the active condition. Active iron, in dissolving, sends almost exclusively ferrous ions into solution, and it would be anticipated from the usual formula for expressing the single potential that it would be more strongly negative in a ferric than in a ferrous solution. Actually the reverse is the case, and the following explanation is suggested. Since iron sends almost exclusively ferrous ions into solution, the solution with which iron is in electromotive equilibrium must likewise contain almost exclusively ferrous ions. When immersed in a ferric solution, iron tends to alter the composition of the solution so as to make it approach that of a solution in electromotive equilibrium with the metal, that is, the iron sends ferrous ions into the solution with a velocity greater than that with which ionic equilibrium in the iron is established; hence there is a concentration of ferric ions at the surface of the iron, and the potential becomes more positive.

G. F. M.

"Galvanic" Corrosion of Iron in Water by means of Copper–Zinc Alloys. W. P. JORISSEN (*Chem. Weekblad*, 1916, **13**, 1020—1025).—A summary of work published more than fifty years ago on the corrosion of iron by water in presence of brass.

A. J. W.

Mixed Crystals of Ammonium Chloride and Ferric Chloride. ALBERT RITZEL (*Jahbr. Min.*, 1916, i, Ref. 287; from *Chemie der Erde*, 1914, **1**, 9—48).—The results of numerous experiments are stated, but no definite conclusion is arrived at, beyond the suggestion that adsorption appears to play an important part. Other conditions being equal, the amount of ferric chloride taken up by the ammonium chloride depends on the degree of supersaturation of the liquid, that is, on the velocity of crystallisation. L. J. S.

Formation of Mixed Crystals. ALBERT RITZEL (*Jahrb. Min.*, 1916, i, Ref. 288; from *Chemie der Erde*, 1915, **1**, 270—293).—The composition of mixed crystals of potassium and ammonium chlorides, of potassium and ammonium sulphates, and of copper and zinc sulphates depends on the degree of supersaturation of the liquid, that is, on the velocity of crystallisation. It is therefore suggested that adsorption plays a part, as in the mixed crystals of ammonium and ferric chlorides (see preceding abstract).

L. J. S.

Effect of the Addition of Alkali to Sea-water on the Hydrogen Ion Concentration. A. R. HAAS (*J. Biol. Chem.*, 1916, **26**, 515—517).—On adding sodium hydroxide to sea-water, the hydroxyl ion concentration at first rises rapidly and then very slowly until the magnesium hydroxide has all been precipitated. After this, further additions of the alkali cause a more rapid rise in the concentration of the hydroxyl ion, but this rise is again soon checked by the precipitation of calcium hydroxide. After the calcium hydroxide is all precipitated, further addition of alkali causes a corresponding increase in the concentration of the hydroxyl ion. H. W. B.

Mineralogical Chemistry.

Chemical Composition of a Sulpho-salt from S. Giorgio (Sardinia). PROBO COMUCCI (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 111—114).—The mineral here described occurred as a small, lenticular mass enclosed in the silurian schist, and forms a lead-grey mass with metallic lustre and lamellar-fibrous structure. Its percentage composition is: S, 21·54; Fe, 3·99; Pb, 37·86; and Sb, 36·01, which agrees satisfactorily with the formula $15Sb_2S_3,18PbS,7FeS$. If the iron is regarded as replacing the

lead, the mineral appears to be a solid solution of 1 mol. of zinckenite, $(Pb,Fe)S,Sb_2S_3$, with 2 mols. of jamesonite, $2(Pb,Fe)S,Sb_2S_3$; the value of D, namely 5·65, is, indeed, intermediate between those of these two minerals, 5·3 and 5·8. No crystallographic measurements were possible. T. H. P.

New Zinc Phosphates from Salmo, British Columbia. ALEXANDER H. PHILLIPS (*Amer. J. Sci.*, 1916, [iv], **42**, 275—278). —A large cavity in zinc carbonate ore in the Hudson Bay mine, near Salmo, contains stalactitic masses of hemimorphite and spencerite. The latter, a new species described by T. L. Walker (1916), presenting the form of white, corroded crystals with a strong, pearly lustre on the good cleavage, gave analysis I, agreeing with the formula $Zn_3(PO_4)_2,Zn(OH)_2,3H_2O$, that is, a basic zinc phosphate like tarbuttite (A., 1908, ii, 397) with the addition of water of crystallisation.

	ZnO.	P_2O_5.	H_2O.	Total.	Sp. gr.
I.	60·39	26·13	13·44	99·96	3·123
II.	57·55	28·82	13·71	100·08	3·213

Embedded in the spencerite are orthorhombic crystals identical in habit, angles ($a:b:c=0·589:1:0·488$), cleavages, and optical characters with hopeite. These crystals, to which the name *hibbenite* is applied, gave analysis II (mean of two analyses made on the same sample of several crystals), agreeing with the formula $2Zn_3(PO_4)_2,Zn(OH)_2,6\frac{1}{2}H_2O$. Attached to the surface of these crystals of hibbenite are minute lenticular crystals, which perhaps represent still another new basic zinc phosphate. L. J. S.

Ambatoarinite, a New Mineral from Madagascar. A. LACROIX (*Bull. Soc. franç. Min.*, 1915 [that is, 1916], **38**, 265—271).—The crystalline limestones near Ambatoarina, between Ambositra and Ambatofangehana, contain in certain bands, in addition to calcite, abundance of silicates, including imerinite (a new type of soda-amphibole), microcline, albite, etc. Small, transparent, yellow crystals of monazite are also present—an unusual mode of occurrence of this mineral; it has D 5·25, and contains (anal. I by Pisani) very little thoria. In other bands, less rich in silicates, a magnesian calcite is associated with celestite, microcline, galena, and the new mineral ambatoarinite. This dense rock was crushed and the heavier constituents separated in methylene iodide; the heavy residue was purified from traces of calcite by treatment with acetic acid, and of the remainder 19% dissolved with effervescence in hydrochloric acid; this portion gave analysis II, corresponding with the formula $5SrCO_3,4(Ce,La,Di)_2(CO_3)_3,(Ce,La,Di)_2O_3$. The mineral has a higher birefringence (about 0·08) and refractive indices (mean 1·658) than celestite, which it closely resembles in general appearance. It is orthorhombic with a prism angle of 85°; the optic axial plane is parallel to (010), and the optic sign negative. The mineral thus differs from ancylite, the only known

double carbonate of strontium and cerium, which is hydrated and optically positive.

	CO_2.	P_2O_5.	ThO_2.	Ce_2O_3.	$(La,Di)_2O_3$.	Fe_2O_3.	CaO.	SrO.	Loss on Ignition.	Total.
I.	–	30·18	1·05	39·51	27·80	0·92	0·46	—	0·47	100·39
II.	25·4	—	—	34·1	22·7	—	—	17·8	–	100·0

The development in the crystalline limestones of all these minerals indicates that the process of metamorphism must have been accompanied by the introduction of more chemical material.

L. J. S.

The Limits of Mixed Crystals in Muscovite and Biotite. H. E. Boeke (*Jahrb. Min.*, 1916, i, 83—117).—The results of 207 published analyses of muscovite and biotite are quoted and reduced to molecular percentages of SiO_2+TiO_2, R_2O, RO, and R_2O_3. These are plotted from the four corners of a regular tetrahedron (A., 1914, ii, 283), and the points representing each analysis are projected on two planes at right angles. They fall into two more or less defined areas around the line between the points given by $R_2O,R_2O_3,2SiO_2$ and $2RO,SiO_2$ on the tetrahedron, that belonging to biotite being rather more diffuse and irregular. L. J. S.

The General Application of the Regular Tetrahedron for the Representation of Four-component Systems: Application to Alkali and Aluminous Amphiboles. H. E. Boeke (*Jahrb. Min.*, 1916, i, 118—125).—Plotting the molecular percentages of SiO_2, R_2O, RO, and R_2O_3 from the four corners of a regular tetrahedron, and projecting the points on planes at right angles lying in the zones between the faces of the tetrahedron, was a method employed with the aluminous augites (A., 1914, ii, 283) and micas (preceding abstract). A general formula is now given for projecting on any desired plane, and the same applied to represent the composition of the alkali and aluminous amphiboles. L. J. S.

Analytical Chemistry.

Sulphonephthaleins as Indicators for the Colorimetric Estimation of Hydrogen Ion Concentration. HERBERT A. LUBS and WILLIAM MANSFIELD CLARK (*J. Washington Acad. Sci.*, 1916, **6**, 481—483).—In addition to the indicators mentioned in a previous paper (this vol., ii, 44), the authors mention that dibromo-*o*-cresol-sulphonephthalein (P_{H}^{+} 5·2—P_{H}^{+} 6·8) is useful for the purpose. The bromothymolsulphonephthalein described previously is really a dibromo-compound. W. P. S.

Colorimetric Estimation of the Hydrogen Ion Concentration of Bacteriological Culture Media. WILLIAM MANSFIELD CLARK and HERBERT A. LUBS (*J. Washington Acad. Sci.*, 1916, **6**, 483—489).—The authors have tested the applicability of a set of indicators to solutions such as are used in bacteriological work; the indicators (compare this vol., ii, 44) have a useful range from about $P_{\overset{+}{H}}$ 1·0 (thymolsulphonephthalein, acid range) to $P_{\overset{+}{H}}$ 10·0 (o-cresolphthalein). W. P. S.

Petrographic Microscope in Analysis. F. E. WRIGHT (*J. Amer. Chem. Soc.*, 1916, **38**, 1647—1658).—Attention is directed to the usefulness of the petrographic microscope in the study of certain chemical problems, and the methods of determining optical properties by its means are described. The instrument may be of service in the identification of compounds, such as osazones and alkaloids, in the determination of the homogeneity of materials, and in the examination of various commercial products. It has been employed by Rankin and Wright (A., 1915, ii, 50) for determining the phase relations in the system $CaO–Al_2O_3–SiO_2$. E. G.

Sodium Pyrogallate as a Reagent for the Estimation of Oxygen. J. W. SHIPLEY (*J. Amer. Chem. Soc.*, 1916, **38**, 1687—1701). —An account is given of a study of sodium pyrogallate as a substitute for the potassium salt in the estimation of oxygen in mixtures of gases. A special pipette is described which outwardly resembles the Richard pipette and inwardly the Orsat pipette. It was found that complete absorption of oxygen could be secured in four minutes by means of solutions containing pyrogallol, sodium hydroxide, and water in varying proportions. In using this reagent, no carbon monoxide was obtained. A solution, containing sodium hydroxide, pyrogallol, and water in the proportions by weight, 7·36 : 10·0 : 11·62, was found to have five times the specific absorptive power of the potassium pyrogallate solution recommended as the best by Anderson (A., 1915, ii, 647). The total volume of oxygen absorbed was rather more than 3 atoms to 1 mol. of pyrogallol. Experiments made with ammonium and barium pyrogallates showed that these substances are unsuitable for general use in gas analysis. E. G.

Rapid Estimation of Sulphur in Coal Gas. F. MYLIUS and C. HÜTTNER (*Ber.*, 1916, **49**, 1428—1443).—A full account is given of a method for estimating the total sulphur in about 200 c.c. of gas, and in about half an hour, with the same degree of accuracy as most of the usual methods. The gas is driven at a steady rate from a gas burette into a small mixing chamber arranged on the principle of the Bunsen burner, into which air is drawn by an aspirator, and the mixture of air and gas (about six times as much air as gas) is led into a small quartz tube, where it meets a roll of thin platinum gauze about 5 mm. long, followed by a roll of platinum fabric, woven of very thin wire, about 15 cm. long. Combustion takes place over a short length of the platinum,

the complete oxidation of sulphur dioxide is finished over another short region, whilst the remaining length serves to trap the sulphuric acid spray, for which purpose the fine metal is very suitable. After all the gas has been burnt, the tube is rinsed out and the sulphuric acid is titrated with 0·001*N*-sodium carbonate, using ethereal iodoeosin as the indicator. A correction usually has to be made for the alkalinity of the wash-water, the volume of which should be about 20 c.c.

It is found that the sulphur content of the gas as drawn from the main varies from hour to hour, according to the temperature. The removal of the carburetting substances, as is being done during the war, has the welcome effect of considerably lowering the amount of sulphur compounds. Experiments have also been conducted on a small scale in order to find absorbents for the sulphur compounds, and phenylhydrazine is shown to be most efficient.

For qualitative purposes, the method of combustion in contact with porous platinum can be applied to 10 c.c. of gas. J. C. W.

Volumetric Studies. HENRIK ENELL (*Zeitsch. anal. Chem.*, 1916, **55**, 452—459).—Iodoeosin and dimethylaminoazobenzene were found to be suitable indicators for use in the presence of hydrogen peroxide, and are preferable to phenolphthalein. They may be used for the estimation of sodium in sodium diethylbarbiturate (sodium-veronal), since they are not affected by free diethylbarbituric acid. In the titration of hydrogen sulphide solution with silver nitrate solution it is recommended that a definite quantity of sodium chloride solution be also added; the silver chloride formed causes the complete precipitation of the colloidal silver sulphide, and the excess of silver nitrate added is then titrated after the silver chloride and sulphide have been removed by filtration. Attention is directed to the fact that a very stable solution is obtained when hydrogen sulphide is dissolved in a mixture of equal volumes of glycerol and water. Alcohol (96% by vol.) dissolves 8·26 times its vol. of hydrogen sulphide, but the solution gradually decomposes with the deposition of sulphur crystals. One vol. of ether dissolves 14·46 vols. of hydrogen sulphide; after three months the solution still contains 13·7 vols. of the gas. W. P. S.

Estimation of Thiosulphate Sulphur in Lime-Sulphur Solutions by Iodine. PHILIP L. BLUMENTHAL and S. D. AVERITT (*J. Amer. Chem. Soc.*, 1916, **38**, 1701—1704).—Averitt (this vol., ii, 488) has shown that the substance titrated with iodine after the removal of polysulphides from a lime-sulphur solution is thiosulphate. This was effected by a process in which tetrathionate was reconverted into thiosulphate and estimated. The accuracy of this method for estimating the thiosulphate has now been confirmed by converting the tetrathionate into sulphate by oxidation and comparing the weight of barium sulphate obtained from such solutions with the value obtained by titration. The results prove that the iodine values obtained by titration, after the decomposi-

tion of the polysulphides with hydrochloric acid, do actually represent thiosulphate.

It has been found that excess of iodine does not react with tetrathionate when left in neutral or slightly acid solutions. In the titration of lime–sulphur solutions with iodine, a little sulphate is always produced, but the quantity of iodine used to form sulphate in an ordinary titration is too small to cause an appreciable error in the estimation of thiosulphate. E. G.

Estimation of Nitrogen by Direct Nesslerisation. I. Total Nitrogen in Urine. Otto Folin and W. Denis (*J. Biol. Chem.*, 1916, **26**, 473—480).—The urine is first diluted so that 1 c.c. contains from 0·7 to 1·5 mg. of nitrogen. For practical purposes, when the density is 1·018 or under, the urine should be diluted one in five; between 1·018 and 1·030, one in ten; and above 1·030, one in twenty. One c.c. of the diluted urine is measured by an Ostwald pipette into a silica or a hard glass test-tube (190 mm. × 15 mm.). With an ordinary pipette is added 1 c.c. of a filtered mixture of phosphoric and sulphuric acids containing 1 vol. of concentrated sulphuric acid, 3 vols. of concentrated phosphoric acid (85%), and one-fifteenth volume of a 10% solution of crystallised copper sulphate, together with a quartz pebble or piece of granite to prevent bumping.

The mixture is now heated over a microburner, with the bottom of the test-tube within 1 cm. of the top of the burner, until nearly all the water has been driven off, as indicated by the absence of foam and the appearance of dense sulphuric acid fumes within the test-tube. This should occur in two to five minutes. The mouth of the test-tube is covered with a watch-glass, and the heating continued for two to four minutes, when the liquid should be clear and blue, green, or light yellow in colour. During this time the flame must be so regulated that only a little of the acid fumes escapes from the test-tube.

After cooling, the contents of the test-tube are washed with 125 c.c. of water into a 250 c.c. measuring flask, and an amount of 10% sodium hydroxide solution added equivalent to 11/8 times the titratable acid content of 1 c.c. of the phosphoric–sulphuric acid mixture (phenolphthalein as indicator), together with an extra 2 c.c. of the alkali to ensure alkalinity. Into another 250 c.c. flask 1 c.c. of the acid mixture and 20 c.c. of a standard ammonium sulphate solution (containing 1 mg. of nitrogen in 20 c.c.) are introduced, and then 125 c.c. of water and the same amount of sodium hydroxide solution as in the case of the unknown. To each flask, 15 c.c. of a modified Nessler solution is added, the contents quickly mixed, and then brought to the mark with water. After again mixing, the liquids are either centrifugalised or filtered through a small cotton plug, and the solutions thus obtained, which must be crystal-clear, compared in a Duboscq colorimeter in the usual way. If the sediment obtained after nesslerisation is mixed with a red deposit, the process must be repeated.

The modified Nessler's solution is prepared by dissolving

approximately 75 grams of potassium iodide in 50 c.c. of warm water, adding 100 grams of mercuric iodide, stirring, diluting with water to a litre, and filtering. To 300 c.c. of the filtrate 200 c.c. of 10% sodium hydroxide solution and 500 c.c. of water are added and mixed.

The new method, which is very quick and in which the distillation of the ammonia is avoided, gives results which agree closely with those obtained by the ordinary Kjeldahl method. H. W. B.

Estimation of Nitrogen by Direct Nesslerisation. II. Non-protein Nitrogen in Blood. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1916, **26**, 491—496. Compare preceding abstract).—In this method the blood proteins are precipitated by metaphosphoric acid. The metaphosphoric acid solution should be freshly prepared by dissolving sticks of so-called "glacial phosphoric acid" in cold water. Solution takes place slowly, and the resulting solution changes in about three days into orthophosphoric acid, and loses thereby its precipitating power.

To about 20 c.c. of water in a 50 c.c. measuring flask 5 c.c. of blood and then 3 c.c. of 25% metaphosphoric acid are added, mixed thoroughly, and after remaining for one to twenty-four hours, filled up to the mark with water, mixed, and filtered; 10 c.c. of the filtrate are then digested with the phosphoric–sulphuric acid mixture as in the method for the estimation of nitrogen in urine (*loc. cit.*). The resulting liquid is made up to 100 c.c. instead of to 250 c.c., and compared with a standard solution containing 0·5 mg. of nitrogen diluted after nesslerisation to 100 c.c.

H. W. B.

Estimation of Nitrogen by Direct Nesslerisation. III. Ammonia in Urine. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1916, **26**, 497—499. Compare preceding abstracts).—In this new method the uric acid, the phenols, and 90% of the creatinine in urine are removed by blood charcoal, and the ammonia then estimated by direct nesslerisation.

To 10 c.c. of urine in a large test-tube or small flask there are added 1 c.c. of 25% metaphosphoric acid, 9 c.c. of water, and 2 grams of blood-charcoal (free from ammonia). It is shaken for at least one minute, and filtered through a dry filter-paper. One to 5 c.c. of the filtrate is transferred to a 100 c.c. measuring flask, about 70 c.c. of water added, and then 15 c.c. of the modified Nessler's solution (*loc. cit.*). It is then made up to volume with water, mixed, and compared in the usual manner with the colour obtained by nesslerising 1 mg. of ammonia nitrogen in another 100 c.c. flask.

This new, simple method appears to give absolutely trustworthy results for the ammonia of urine. H. W. B.

Estimation of Nitrogen by Direct Nesslerisation. IV. Urea in Urine. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1916, **26**, 501—503. Compare preceding abstracts).—The urea is hydrolysed

by urease, and the latter then removed from the solution by treatment with metaphosphoric acid. The total ammonia is subsequently estimated by direct nesslerisation. The urease may be used in the form of commercial "soja bean meal."

For the estimation, 1 c.c. of the urine is transferred by means of an Ostwald pipette to a 100 c.c. volumetric flask, 0·1 to 0·25 gram of soja bean meal added in the form of a 1% suspension in 20% alcohol, the flask stoppered and allowed to remain for one hour at the ordinary temperature or for fifteen minutes in a water-bath at about 50°. Twenty-five c.c. of water and 1 c.c. of fresh 25% metaphosphoric acid are added and mixed; about 1 gram of blood-charcoal and 25 c.c. more of water are then added, shaken, made up to volume, mixed, and filtered through a dry filter-paper. From 5 to 20 c.c. of the filtrate are then nesslerised and compared with a standard in the usual way. The results are identical with those obtained by the Marshall-Van Slyke method. H. W. B.

Estimation of Nitrogen by Direct Nesslerisation. V. Urea in Blood. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1916, **26**, 505—506. Compare preceding abstracts).—The method is similar to that described for the estimation of urea in urine. About 0·1 gram of soja bean meal in the form of a 1% suspension is added to 5 c.c. of fresh oxalated blood in a 50 c.c. volumetric flask. After remaining for one hour, 25 c.c. of water and 2 c.c. of fresh 25% metaphosphoric acid are added, and then water to the mark. After mixing and leaving at least forty-five minutes, the liquid is filtered and the filtrate shaken with 0·5 gram of blood-charcoal. After again filtering, 10 c.c. is transferred to a 25 c.c. volumetric flask, 5 c.c. of the modified Nessler's solution added, mixed, and made to volume. The colour is compared at once (within ten minutes) with a standard prepared by nesslerising 0·25 mg. of ammonia nitrogen in a 50 c.c. flask with 10 c.c. of the modified Nessler's reagent. H. W. B.

The Estimation of Ammonia in Human Urine. Comparative Estimations with the Apparatus of Schlœsing, Krüger–Reich–Schittenhelm, and of Hahn. CH. SCHENITZKY (*Biochem. Zeitsch.*, 1916, **76**, 177—186).—In the apparatus of Schlœsing, the ammonia is distilled off at the ordinary temperature in a desiccator over standard acid; in that of Krüger, Reich, and Schittenhelm the ammonia is distilled off from a flask warmed in a bath at about 43°. Hahn's method (*Med. Klin.*, 1913, **39**, 1598) is a modification of this, in which the neck of the distillation flask is cooled with ice. In this apparatus, the distillation of ammonia is said to take less time, but the author finds that it is not safe to discontinue the distillation after such a short period as that recommended by Hahn. He does not find there is any advantage in using Hahn's modification. By Schlœsing's method the distillation of the ammonia takes, in the case at any rate of urines rich in ammonia, not less than eight days. The author recommends the Krüger-Reich-Schittenhelm method. S. B. S.

Titrimetric Estimation of Nitrites. B. S. DAVISSON (*J. Amer. Chem. Soc.*, 1916, **38**, 1683—1687).—In order to find a suitable method for the estimation of nitrites in a study of the nitrification of soils, the various methods hitherto described were tested, and a modification of Chabier's iodometric process was finally adopted.

The apparatus employed consists of a wide-mouthed Erlenmeyer flask with a side-tube, for the admission of gas, which leads to the bottom and bears an arm parallel to the base of the flask and furnished with several holes on each side to allow the rapid passage of gas through the liquid in the flask. The flask is provided with a rubber stopper carrying an outlet tube for the gas, a separatory funnel for introducing the acid, a burette for standard thiosulphate solution, and a second burette for standard nitrite solution for titrating back if necessary. The solution of the nitrite is placed in the flask and diluted to about 150 c.c. Potassium iodide (0·5 gram) and 2 c.c. of starch solution are added. The stopper is then inserted and a current of carbon dioxide is passed through the flask for three minutes. The rate of passage of the gas is then reduced and 10 c.c. of 15% sulphuric acid are introduced. The mixture is left for a short time and then titrated with standard thiosulphate.

The method gives accurate results and is but little affected by the organic matter in soil extracts. E. G.

The Estimation of Phosphoric Acid in Plant Material. AS. ZLATAROFF (*Biochem. Zeitsch.*, 1916, **76**, 218—231).—In direct ashing of the material there is a danger of loss by volatilisation of phosphoric acid, which is increased when sulphuric acid is added. Volatilisation of phosphoric acid is inhibited by the presence of carbonates. The wet-ashing process of Neumann gives the best results. Satisfactory results are also obtained by the citrate method. S. B. S.

Oxygen-consuming Power of Natural Waters. GEORGE W. HEISE and R. H. AGUILAR (*Philippine J. Sci.*, 1916, *A*, **11**, 37—47).—In estimating the oxygen-consuming power of waters by means of potassium permanganate in acid solution, it is essential to have identical conditions as regards time and temperature. The effect of chlorides is diminished by employing low temperatures and by employing alkaline, instead of acid, permanganate, the final titration being made with thiosulphate. Hypochlorites should be destroyed before making the estimation.

The method, being uncertain, is only of much value when a water supply has to be examined repeatedly. N. H. J. M.

Electro-analysis of Silver with Solutions of Silver Chloride in Ammonia. E. P. SCHOCH and F. M. CRAWFORD (*J. Amer. Chem. Soc.*, 1916, **38**, 1682—1683).—A method of estimating silver by electrodeposition from solutions of silver chloride in ammonia has been devised. This electrolyte is superior to the cyanide electrolyte, since it yields pure deposits, whilst the latter gives

impure deposits. Estimations have been carried out in the following manner by means of the apparatus described by Schoch and Brown (this vol., ii, 578). Samples of pure sheet silver were dissolved in concentrated nitric acid, and the silver was precipitated with a slight excess of hydrochloric acid. In some experiments the silver chloride was collected, washed, and dissolved in excess of concentrated ammonia, whilst in others the original mixture was treated with ammonia. In each case about 20 grams of ammonium chloride were added, the mixture was diluted to about 150 c.c., and submitted to electrolysis at the ordinary temperature with an initial current of 0·35 ampere (which required 1·1 volts between the electrodes). The voltage was kept constant until the current had fallen to zero, and was then allowed to rise gradually to 1·3—1·4 volts, and the electrolysis continued for a total of twenty-five to thirty minutes. Oxalic acid (3 grams) was then added, and sufficient hydrochloric acid to render the solution faintly acid to litmus-paper. Electrolysis was then continued for about twenty minutes, and the electrodes were washed and dried. The method was found to give very accurate results. E. G.

Estimation of Silver in Protein Preparations. HUGO WASTENSON (*Chem. Zentr.*, 1916, i, 810; from *Pharm. Post*, 1916, **49**, 187—188).—A method is described for the estimation of silver in protein preparations (for example, *Argentum proteinicum*) which also contain chlorides. From 0·2 to 0·5 gram of the substance is heated with 10 c.c. of concentrated sulphuric acid and 2 c.c. of concentrated nitric acid until nitrous fumes cease to appear; after cooling, the mixture is diluted with 25 c.c. of water, heated until the water has been evaporated, and the heating then continued for a further thirty minutes. The clear solution is now diluted with water to about 100 c.c. and titrated with $N/10$-ammonium thiocyanate solution in the presence of ferric alum.
W. P. S.

Estimation of Total Hardness (in Waters) by Potassium Palmitate according to Blacher's Method. M. TILGNER (*Chem. Zeit.*, 1916, **40**, 675. Compare A., 1913, ii, 153).—Owing to the difficulty of ascertaining the point when the carbon dioxide has been expelled from the water after the temporary hardness has been titrated with hydrochloric acid, it is better to neutralise the free carbon dioxide with $N/10$-potassium hydroxide solution, using phenolphthalein as indicator. The total hardness is then titrated with potassium palmitate solution as described (*loc. cit.*).
W. P. S.

Chemical Analysis of Gypsum. ALFREDO CAVAZZI (*Ann. Chim. Applicata*, 1916, **6**, 18—26).—Details are given of methods for the estimation of (1) sodium chloride in crude or burnt gypsum, (2) sodium sulphate in crude gypsum, volumetrically and gravimetrically, (3) magnesium sulphate, and (4) carbon dioxide, in

crude gypsum, (5) free lime in burnt gypsum, and (6) silica, alumina, lime, and magnesia as carbonates and ferric oxide in the crude mineral. T. H. P.

Estimation of Zinc by Schaffner's Method. JOSEF PATEK (*Zeitsch. anal. Chem.*, 1916, **55**, 427—452).—A critical examination of this method (titration with sodium sulphide solution). It is found that it is not necessary to have exactly the same weights of zinc in the test solution and in the standard comparison solution, and that the presence of ammonium salts in the solutions does not affect the trustworthiness of the results (compare A., 1907, ii, 301). Nitric acid, sulphuric acid, or hydrochloric acid may be used to dissolve the zinc, and it is immaterial whether the iron present is oxidised with bromine or hydrogen peroxide. In neutral or ammoniacal solution, freshly precipitated zinc sulphide does not react with ammonium salts with the formation of ammonium sulphide (compare A., 1907, ii, 53). W. P. S.

Electro-analytical Method for the Estimation and Separation of the Metals of the Copper–Tin Group. EUGENE P. SCHOCH, DENTÓN J. BROWN, and. in part, THOMAS E. PHIPPS (*J. Amer. Chem. Soc.*, 1916, **38**, 1660—1681).—It is usually considered that solutions of chlorides are not suitable for the electro-analytical deposition of metals owing to the oxidising action of the liberated chlorine. Since such solutions, however, present all the advantages of simple acid electrolytes and the formation of chlorine can be prevented by the addition of reducing agents, an investigation has been made of their use with the common metals, and especially with bismuth, antimony, and tin. It has been found that antimony, bismuth, copper, lead, tin, and cadmium can be deposited quantitatively and in good form from hydrochloric acid solutions if suitable reducing agents are present and oxides of nitrogen and nitric acid are absent, and that such electrolytes permit of the separation of all these metals from each other and from other metals of the copper–tin group.

The Sand-Fischer apparatus and electrodes were employed. The electrodes were composed of fine platinum wire gauze, and the total surface of the cathode was about 90 sq. cm. A tall, narrow beaker of 350 c.c. capacity was used, the volume of electrolyte required to cover the electrodes being about 150 c.c. The normal calomel electrode was employed as the auxiliary electrode. In the estimation of metals which form alloys with platinum, the cathode was covered with a deposit of copper before the deposition of the metal. A stirrer making 800 revolutions per minute was used.

In preparing the electrolyte, a sample is taken sufficient to give a deposit of at least 0·1 gram of any constituent, but insufficient to give a total of any single deposit of more than 0·66 gram. The weighed sample is treated with 8—12 c.c. of concentrated hydrochloric acid (D 1·20) and an equal volume of water. Samples consisting of two or more reactive metals are dissolved by being placed in contact with platinum, but if lead or more noble metals

are present, a few drops of nitric acid are added and the mixture is warmed slightly. The solution is then treated with 2 grams of hydroxylamine hydrochloride, and the mixture again warmed and diluted to 150—200 c.c.

An outline is given of a scheme for the systematic separation of all the common metals of the copper–tin group. If arsenic is present, the amount of hydroxylamine hydrochloride added should be 3 grams, and the mixture should be distilled from a 200 c.c. distilling flask, through which a current of hydrogen chloride is passed, in order to remove the arsenic as arsenious chloride. The distillation is continued until the residue in the flask is reduced to 10—20 c.c. This residue is rinsed into the electrolysis beaker and diluted to 150—200 c.c. If, however, a precipitate of mercurous chloride, silver chloride, gold, or platinum is present, the concentrated mixture is somewhat diluted, filtered, the residue washed, and the filtrate and washings are then diluted to 150—200 c.c. If the precipitate contains silver chloride, it is treated with ammonia; the silver can be deposited quantitatively from this solution by Schoch and Crawford's method (this vol., ii, 577). Any mercurous chloride, gold, or platinum may be separated and estimated by the usual methods.

From the filtered and diluted solution the first metals deposited with the least *E.M.F.* are bismuth, copper, and antimony. After these have been removed, the next metals deposited are tin and lead, and subsequently cadmium is deposited. A detailed account of the electrolytic separation and estimation of these metals is given in the original. E. G.

Volumetric Estimation of Lead. JOHN WADDELL (*Analyst*, 1916, **41**, 270—272).—A detailed description is given of the application of the chromate method to the estimation of lead in ores. The lead is obtained in solution as chloride, and precipitated as chromate; this is dissolved in hydrochloric acid, potassium iodide is added, and the liberated iodine titrated with thiosulphate solution. For the estimation of galena in calcite, the ore is boiled with hydrochloric acid, nitric acid is then added, the mixture concentrated, treated with ammonia, then with acetic acid and ammonium acetate, and the lead precipitated by the addition of potassium chromate to the hot solution. If the ore under examination contains antimony, bismuth, silver, or decomposable silicates, the lead is separated as sulphate, then dissolved in ammonium acetate, and precipitated as chromate. W. P. S.

Volumetric Estimation of Mercury Salts. Evaluation of Mercuric Chloride Compresses. G. ADANTI (*Boll. chim. farm.*, 1916, **55**, 553—554).—This method is based on the reduction of mercury salts to metallic mercury by means of formaldehyde in presence of potassium hydroxide. The mercury is treated with excess of a standard iodine solution, the excess of the latter over the amount required to convert the mercury into mercuric iodide being determined by titration with standard sodium thiosulphate

solution. The method is rapid and gives very exact results, and is carried out as follows.

One gram of the mercuric salt or of the mercuric chloride compress is treated in a 250 c.c. flask or cylinder with a little water and, if necessary, sodium chloride to dissolve the mercuric salt, the solution being made up to volume. Fifty c.c. of the liquid are mixed in a beaker with 5 c.c. of ordinary formalin (about 40% aqueous formaldehyde solution) and 10 c.c. of 33% sodium or potassium hydroxide solution, and the whole heated on a water-bath for a few minutes and then allowed to cool. The liquid is then neutralised with acetic acid and the precipitated mercury collected and washed. Filter and precipitate are shaken with 100 c.c. of water slightly acidified with acetic acid and exactly 20 c.c. of decinormal iodine solution until all the mercury has passed into solution as mercuric iodide and the excess of iodine estimated; 1 c.c. of $N/10$-iodine = 0·01 gram of mercury or 0·01355 gram of mercuric chloride. T. H. P.

Analysis of Forrocerium. LAUREANO MENÉNDEZ (*Anal. Fis. Quim.*, 1916, **14**, 401—402).—The mixture can be precipitated as $Fe_2O_3 + CeO_2$, in which the iron can be determined directly, and the cerium by difference. A. J. W.

Detection of Nickel in Cobalt Salts. A. R. MIDDLETON and H. L. MILLER (*J. Amer. Chem. Soc.*, 1916, **38**, 1705—1711).—Tschugaev (A., 1905, ii, 613) has shown that nickel can be readily detected by means of the scarlet precipitate produced when a nickel solution is boiled with a little dimethylglyoxime in presence of excess of ammonia or sodium acetate. This test has not been found entirely satisfactory for the detection of traces of nickel in cobalt salts, and the following method has therefore been devised.

The solution of the cobalt salt containing nickel is treated with 10% solution of potassium cyanide until the precipitate is just dissolved, and the solution is then heated and shaken for five minutes after it changes colour. The solution is diluted to 50 c.c. with water at 85°, 1 c.c. of dimethylglyoxime solution (1%) is added, and silver nitrate (1%) is added drop by drop with constant stirring until a permanent precipitate is produced. After the mixture has been left for a period of from one to twenty-four hours, the pink colour of the nickel compound appears. This method can be employed when large quantities of cobalt are present; it increases the ordinary sensitiveness of dimethylglyoxime about eight times, and is capable of detecting less than 0·002 mg. of nickel in a volume of 50 c.c. E. G.

The Use of Diphenylglyoxime as an Indicator in the Volumetric Estimation of Nickel by Frevert's Method. G. L. KELLEY and J. B. CONANT (*J. Ind. Eng. Chem.*, 1916, **8**, 804—807).—Certain modifications are suggested in Frevert's volumetric method for the estimation of nickel; the procedure is now as follows: The sample is dissolved in 50 c.c. of hot dilute nitric acid,

or in hot dilute hydrochloric acid if it contains more than 0·5% of chromium, and the iron and carbides are oxidised with nitric acid, and the solution finally boiled to expel the products of its decomposition. To the cooled solution citric acid, dimethylglyoxime solution, and sufficient ammonia to render alkaline are added, and after a time the precipitate is filtered off through an asbestos bed, and thoroughly washed. It is then treated on the filter with nitric acid, and the solution and washings, containing the nickel, are boiled to half bulk with a little potassium chlorate to decompose dimethylglyoxime in the solution, and then slightly more than neutralised with ammonia. The resulting liquid, which should measure about 250 c.c., is then titrated with potassium cyanide, using silver iodide as indicator, the titre value of which is determined by means of a blank, the end-point in each case being the disappearance of the last trace of turbidity. As an alternative method of titration, the use of a standard nickel sulphate solution and diphenylglyoxime as indicator is recommended. The nickel is dissolved out of the above-mentioned nickel dimethylglyoxime precipitate by means of concentrated hydrochloric acid containing 10% of nitric acid, and the filtrate and washings are evaporated almost to dryness to remove excess of acid, and then diluted to 200 c.c. and rendered slightly alkaline with ammonia (5 c.c. of 1 : 3 solution should be sufficient, otherwise the amount of ammonium salt formed will have an unfavourable effect on the subsequent titration). Standard potassium cyanide solution is then added until the opalescence disappears, after which a further 15 c.c. are run in, followed by 5 c.c. of 0·1% diphenylglyoxime solution in 0·5% sodium hydroxide, and the whole is then titrated back with nickel sulphate until the appearance of a red colour. The method is stated to be rapid and to give accurate results. G. F. M.

Potassium Dichromate as a Standard. II. G. BRUHNS (*J. pr. Chem.*, 1916, [ii], **93**, 312—338. Compare this vol., ii, 337).—Wagner's supposition that potassium dichromate owes its high titration value to the fact that it catalytically promotes oxidation by means of dissolved oxygen does not bear the test of experiment. Two equal volumes of *N*/10-dichromate, one of which has been treated with sodium hydroxide to convert the dichromate into the chromate, are shown, when treated separately and in exactly the same manner with acidified potassium iodide solution in the presence of sodium thiosulphate, to be equivalent to the same amount of thiosulphate within the limit of the experimental error. The same result is attained when the initial solutions are approximately *N*/10-chromate, one of which has been converted into dichromate by the addition of the requisite amount of *N*-hydrochloric acid.

In some experiments Wagner found that the quantity of iodine liberated by potassium dichromate is diminished by about 0·7% when the oxygen had been previously expelled from the solution by carbon dioxide; this diminution is about twice as great as the excess titration value of the dichromate. According to the

author's experience, the diminution does not stand in any relation to the excess value (towards sodium chloride) of the dichromate; he has obtained (1) a diminution of 0·14% in the case of a dichromate the excess value of which was only 0·03%; (2) a diminution of 0·01% with a dichromate, excess value 0·13%; and (3) no diminution at all when the dichromate solution is largely diluted.

The experiments on the subject are being continued.

The author republishes in the paper his experiments (A., 1906, ii, 800) on the time required for the complete separation of the iodine liberated from potassium iodide by very dilute potassium dichromate solution (about 0·002—0·005*N*) in the presence of sulphuric acid and hydrochloric acid respectively. C. S.

Estimation of Tungsten by Fieber's Method. Separation of Tin from Tungsten. E. DITTLER and A. VON GRAFFENRIED (*Chem. Zeit.*, 1916, **40**, 681—682).—This method (A., 1912, ii, 495) is trustworthy for the estimation of tungsten in ferrotungsten; the difference between the results of duplicate estimations does not exceed 0·1%. In the estimation of tungsten in concentrates containing more than 10% of tin, the tungstic acid should be ignited with ammonium chloride in order to remove remaining traces of stannic oxide. A method is described for the estimation of tin in tin ores containing tungsten One gram of the ore is fused with 8 grams of sodium peroxide, the mass is treated with water, diluted to 500 c.c., and filtered; the tungsten is estimated in 250 c.c. of the filtrate by the mercurous nitrate method. A quantity of 200 c.c. of the filtrate is then treated with 10 grams of sodium phosphate and acidified; a small precipitate of silica may form at this point, and is separated by filtration. The solution is then boiled until the peroxide has been decomposed, next treated, while hot, with hydrogen sulphide, the tin sulphide is collected, washed with dilute ammonium acetate solution, and dried. The precipitate may be ignited and weighed as stannic oxide, or the tin may be estimated electrolytically. W. P. S.

Iodometric Estimation of Gold. L. VANINO and F. HARTWAGNER (*Zeitsch. anal. Chem.*, 1916, **55**, 377—388).—Peterson's method (A., 1899, ii, 250) may be rendered more trustworthy by treating the gold chloride ($AuCl_3,HCl$) with a mixture of potassium iodide and potassium iodate, and then titrating the liberated iodine with thiosulphate solution. The reactions are shown by the following equations: $6(AuCl_3,HCl) + 18KI = 6AuI + 6I_2 + 18KCl + 6HCl$;

$$6HCl + 5KI + KIO_3 = 3I_2 + 6KCl + 3H_2O,$$

and $9I_2 + 18Na_2S_2O_3 = 18NaI + 9Na_2S_4O_6$. When applied to quantities of gold chloride containing from 2 to 9 mg. of gold, the error of the method varies from $-0·9$ to $+4·5$%; free acid must not be present in the gold salt. The iodometric method may be applied to the analysis of the salt, $AuCl_3,2H_2O$; the quantity of iodine liberated from potassium iodide by the salt is a measure of the gold content; the difference between this amount of iodine and

that liberated when the salt is treated with a mixture of iodide and iodate indicates the amount, if any, of free hydrochloric acid which may be present (compare also Gooch and Morley, A., 1900, ii, 110). W. P. S.

The Analysis of Benzol First-runnings. Percy E. Spielmann and F. Butler Jones (*J. Soc. Chem. Ind.*, 1916, **35**, 911—912).—Experiments carried out to ascertain whether the method for the analysis of commercial benzols (this vol., ii, 348) was applicable to first runnings indicated that, even with as high a percentage as 65% of carbon disulphide, results were obtained by the distillation test which fell within the limits of accuracy of the earlier benzol analysis. Water-soluble substances were insufficient in quantity to affect the specific gravity, and washing with sulphuric acid likewise caused no alteration. When dealing with a high percentage of carbon disulphide, however, it was found preferable to dilute up to five times the volume with purified benzene. The specific gravity of the paraffin of the first runnings is 0·700, and its percentage is most conveniently obtained by ascertaining the difference between the specific gravity of the benzene–toluene mixture (from the graph previously given, *loc. cit.*) and that of the sample under examination after removal of carbon disulphide, and evaluating by means of a further graph given in the present paper. G. F. M.

Estimation of Naphthalene in Coal Gas. A. J. von Eyndhoven (*Chem. Zentr.*, 1916, i, 858; from *J. Gasbeleuchtung*, 1916, **59**, 107—108).—A few drops of a 1% sodium alizarinsulphonate solution may be used as the indicator in the titration of picric acid with sodium hydroxide solution, as described by Schlumberger (A., 1913, ii, 441). W. P. S.

Estimation of Small Amounts of Ethyl Alcohol and Water in Ethyl Ether for Anæsthesia. Edward Mallinckrodt, jun., and A. D. Alt (*J. Ind. Eng. Chem.*, 1916, **8**, 807—812).—Of the various methods in vogue for the detection of small quantities of water in ethyl ether, only the method of dehydration by potassium carbonate appears to be suitable for a quantitative examination. Experiments made show that water is by its means removed quantitatively from ether containing as much alcohol as is likely to occur in anæsthetic ethers, although when much larger proportions are present dehydration is incomplete. The procedure accordingly consists in shaking 50 c.c. of ether for several hours with 15 grams of potassium carbonate dried at 250°, filtering off the ether, washing out the alcohol from the residue of carbonate with pure, dry ether, drying for one hour at 50°, and weighing, the increase in weight representing the amount of water in the ether. From a determination of the specific gravity of the dehydrated ether thus obtained, the percentage of alcohol which it contains is given by reference to a curve of specific gravities of pure ethyl ether with known admixtures of ethyl alcohol, from

which the following figures may be quoted: for pure ether, D_{25}^{25} 0·70991; with 1% alcohol, D_{25}^{25} 0·71097; with 2% alcohol, D_{25}^{25} 0·71205; 3% alcohol, D_{25}^{25} 0·71303; and 4% alcohol, D_{25}^{25} 0·71424.

G. F. M.

Estimation of Glycerol in Fatty Oils by means of Sodium Glyceroxide. HENRIK BULL (*Chem. Zeit.*, 1916, **40**, 690).—Ten grams of the oil are diluted to 100 c.c. with light petroleum, the solution is treated with 10 c.c. of glycerol–potassium hydroxide solution (20 c.c. of 50% potassium hydroxide solution, 240 c.c. of water, and 240 c.c. of glycerol), and mixed; this treatment removes any free fatty acids in the oil. After settling, 30 c.c. of the clear, light petroleum layer are transferred to a stoppered cylinder, 3 c.c. of sodium ethoxide solution (23 grams of sodium dissolved in 500 c.c. of absolute alcohol) are added, and the mixture is diluted to 50 c.c. with light petroleum. The mixture is shaken and, after a few hours, 25 c.c. of the clear solution are removed, mixed with a small quantity of alcohol, and titrated with *N*/10-hydrochloric acid, using phenolphthalein as indicator. The remaining contents of the cylinder, including the precipitate of sodium glyceroxide, are now rinsed into a flask with 20 c.c. of alcohol, and at once titrated; to avoid the use of a large volume of acid in this titration, 5 c.c. of *N*/2-hydrochloric acid may be added at first, and the titration then completed with *N*/10-acid. The difference (in c.c. of *N*/10-acid) between the two titrations is multiplied by 0·0092 to obtain the quantity of glycerol in 3 grams of the oil. The results obtained by the method agree closely with those found by calculation from the ester numbers of oils.

W. P. S.

Spectroscopic Identification of Phenols. HANS GSELL (*Zeitsch. anal. Chem.*, 1916, **55**, 417—426).—The phenols are converted into their respective phthaleins, the alkali salts of which exhibit characteristic absorption bands. For example, 0·1 gram of resorcinol is mixed with a small quantity of phthalic anhydride and five drops of stannic chloride solution, and the mixture is heated for fifteen minutes at 140°; after cooling, the mixture is dissolved in 5 c.c. of alcohol, 10 c.c. of *N*/2-sodium hydroxide solution are added, the solution is diluted to 1 litre, and examined in the spectroscope. The maximum density of the absorption band for this substance lies between 485 $\mu\mu$ and 492 $\mu\mu$. This position has been determined in the case of some twenty phenols, and varies from 420 $\mu\mu$ for catecholphthalein to 626 $\mu\mu$ for thymolphthalein.

W. P. S.

Arsenotungstic Acid as a Reagent for Phenols. LUIS GUGLIALMELLI (*Anal. Soc. Quim. Argentina*, 1916, **4**, 119—126).—Arsenotungstic acid gives characteristic colorations with many phenols.

A. J. W.

Arsenotungstomolybdic Acid as a Reagent for Phenols. LUIS GUGLIALMELLI (*Anal. Soc. Quim. Argentina*, 1916, **4**, 183—184).—Arsenotungstomolybdic acid is characterised by its power of producing characteristic colorations with many phenols.

A. J. W.

Separation of Cholesterol and *iso*Cholesterol. A. MADINAVEITIA and A. GONZÁLEZ (*Anal. Fis. Quim.*, 1916, **14**, 398—401).—Cholesterol and *iso*cholesterol can be estimated by precipitating the former as a crystalline additive product with oxalic acid, and estimating the latter in the mother liquor as benzoate.

A. J. W.

6-Hydrazino-1-benzoyl-2-methyldihydroindole, a New Reagent for Galactose. J. VON BRAUN (*Ber.*, 1916, **49**, 1266—1268). —See this vol., i, 757.

Examination of Methods for the Detection of Hydrocyanic Acid. G. ANDERSON (*Zeitsch. anal. Chem.*, 1916, **55**, 459—468).—The silver cyanide method (treatment of the cyanide or hydrocyanic acid solution with silver nitrate in the presence of nitric acid) was found to be capable of detecting as little as 0·0039 mg. of cyanogen in 10 c.c. of solution. Previous treatment of the solution with ammonia did not increase the sensitiveness of the test, as stated by Link and Möckel (A., 1879, 402). Equally small quantities of cyanogen could be detected by conversion into thiocyanate and testing for this in the usual way, but the ferrocyanide reaction would not detect less than 0·039 mg. With the *iso*purpurate test (treatment of the cyanide solution with potassium hydroxide and picric acid) in the cold, a red coloration developed after six hours with a solution containing 0·39 mg. of cyanogen, whilst one-tenth of this quantity could be detected by heating the mixture at 50°. The reaction is not, however, very trustworthy (compare A., 1901, ii, 587). The guaiacum–copper sulphate test will detect as little as 0·00039 mg. of cyanogen in 10 c.c. of solution. W. P. S.

Physical Characters and Chemical Reactions of Aspirin. D. E. TSAKALOTOS (*J. Pharm. Chim.*, 1916, [vii], **14**, 174—177. Compare A., 1915, ii, 47, 433).—When aspirin is fused at its melting point and then cooled, it solidifies in a mass which exhibits numerous clusters of concentric rings; if heated slightly above its melting point, it solidifies to a transparent mass. The partial decomposition of aspirin when fused, with the formation of salicylsalicylic acid, affects the melting point of the substance; the author finds that aspirin will melt at 125°, or even lower. Pure aspirin does not give a coloration with ferric chloride, but does so after prolonged contact with water or after having been fused. A green coloration is obtained after a short time when aspirin is treated with vanadic acid reagent (ammonium vanadate dissolved in concentrated sulphuric acid and the solution then diluted with water until the orange colour changes to pale yellow). Aspirin which

has been heated previously just to fusion, at once gives a green coloration with the reagent, whilst a brown coloration is obtained if the aspirin has been more strongly heated. W. P. S.

Determination of the Melting Points of Fats. M. MONHAUPT (*Chem. Zeit.*, 1916, **40**, 676).—A portion of the fat is introduced into a capillary, about 1·5 mm. in diameter, so as to form a layer 6 mm. long about 15 mm. from the lower end of the capillary. This end is then sealed, the layer of fat is melted, and again solidified by placing the capillary on ice. A fine needle is now inserted in the upper end of the capillary; the latter is attached to a thermometer which is immersed in water, and the water is heated gradually. The temperature at which the point of the needle penetrates the fat gives the melting point. W. P. S.

Detection and Estimation of "Saccharin." M. KLOSTERMANN and K. SCHOLTA (*Zeitsch. Nahr. Genussm.*, 1916, **31**, 67—78).—The authors discuss various methods which have been proposed for the detection of "saccharin" in foods, etc., and point out that many of these tests are rendered useless owing to the interference of other substances which may be present. For instance, clove oil, cinnamon oil, salicylaldehyde, gum benzoin, tannin, benzaldehyde, and vanillin all give a coloration with the test described by Kastle (A., 1906, ii, 503). The following test is proposed as being trustworthy. The "saccharin" is extracted from an acid solution of the food by means of a mixture of ether and light petroleum, and the solvent is evaporated. The residue is boiled for ten minutes with 10% hydrochloric acid, and the solution then evaporated to dryness; if this residue has an odour of vanillin, it is extracted several times with a mixture of equal volumes of ether and chloroform, in which the "saccharin" is insoluble. The residue is then treated with phenol, and phosphoric oxide is added. The development of a red-coloured substance which gives a yellow solution with water, changing to bluish-red on the addition of alkali, indicates the presence of "saccharin." Ammonium sulphide discharges the bluish-red colour. Besides vanillin, benzaldehyde is the only substance which gives the reaction, and this aldehyde is expelled during the evaporation with hydrochloric acid or is converted into benzoic acid, which does not interfere. In the method of estimating "saccharin" by fusion with sodium carbonate and potassium nitrate or chlorate, the substance should be hydrolysed with hydrochloric acid, and extracted with a mixture of ether and chloroform in order to remove any *p*-benzoicsulphinide; otherwise, the sulphur contained in this substance would be included in the quantity yielded by the "saccharin." W. P. S.

The Scission of Uric Acid by Soya-bean. HERMANN KUNZ-KRAUSE (*Pharm. Zentr.-h.*, 1916, **57**, 523—525).—In a paper by Wester (this vol., ii, 502) uric acid has been erroneously confused with urea. S. B. S.

Estimation of Carbamide in Urine by means of Urease. BÉLA VON HORVÁTH and HEINRICH KADLETZ (*Chem. Zentr.*, 1916, i, 997—998; from *Deut. med. Woch.*, 1916, **42**, 414—416).—Hahn's

method for the estimation of carbamide by means of urease (A., 1915, ii, 654) gives unsatisfactory results. Urease apparently is uncertain in its action in pure carbamide solution. The ammonia seems to exert a disturbing influence, but it is not possible to work in acid solution, since the reaction is then strongly retarded. On the other hand, good results were obtained by the following modification: 1 c.c. of urine was taken as in Hahn's method, and in the Erlenmeyer flask a small, cylindrical glass vessel of 6 c.c. capacity containing 4 c.c. of *N*/10-hydrochloric acid was suspended, and the flask was well closed. The titration was not carried out until after the lapse of twenty-four hours. Under these conditions clinically utilisable results were obtained. Even with these modifications, however, the method still gave unsatisfactory results with pure carbamide solutions. G. F. M.

Estimation of Dicyanodiamide in Calcium Cyanamide by Caro's Method. G. HAGER and J. KERN (*Zeitsch. angew. Chem.*, 1916, **29**, 309—312).—The results for dicyanodiamide obtained by Caro's method (A., 1911, ii, 162) are too low owing to the fact that a small quantity of dicyanodiamide is precipitated with the silver cyanamide even in the presence of an excess of ammonia, and also because the dicyanodiamide undergoes slight decomposition when the filtrate from the silver cyanamide is boiled with the addition of potassium hydroxide. The error tends to increase with the proportion of dicyanodiamide present. W. P. S.

Influence of the Colour from the Sodium Picrate in the Estimation of Creatinine in Blood and Urine. F. H. MCCRUDDEN and C. S. SARGENT (*J. Biol. Chem.*, 1916, **26**, 527—533).—The authors find that in the estimation of creatinine in the urine by the colorimetric method only two-thirds of the colour produced is due to creatinine, the remaining third being due to picrate. In the case of the blood, the colour due to the creatinine as such is only a small proportion of the total colour produced. The authors consider, therefore, that previous estimations of creatinine in urine, and specially those in blood, are fallacious. H. W. B.

A New Sensitive Reaction for *apo*Morphine. LUCIANO P. J. PALET (*Ann. Soc. Quim. Argentina*, 1916, **4**, 83—86).—With Guglialmelli's arseno-tungstic or arseno-tungsto-molybdic reagent, *apo*morphine gives an indigo-blue coloration; the coloured substance dissolves in amyl alcohol to a solution of the same colour, and in benzene to an intense violet solution. A. J. W.

Estimation of Nicotine in Tobacco. RICHARD KISSLING (*Chem. Zeit.*, 1916, **40**, 594—595).—A criticism of a paper by Baggesgaard-Rasmussen on the same subject (A., 1915, ii, 359). G. F. M.

A New and Delicate Test for Dimethylaminophenyldimethyl*iso*pyrazolone (Pyramidone). LUIS GUGLIALMELLI (*Anal. Soc. Quim. Argentina*, 1916, **4**, 180—182).—Arsenotungstic acid gives with dimethylaminophenyldimethyl*iso*pyrazolone a white pre-

cipitate soluble in alkali with production of an intense blue coloration. Arsenotungstomolybdic acid gives a white precipitate, soluble in alkali to an indigo-blue solution. Both nitric acid and ferric chloride give an indigo-blue coloration. A. J. W.

A New Reaction for Bile Pigments. MORIZ WEISS (*Chem. Zentr.*, 1916, i, 1100—1101; from *Wiener Klin. Woch.*, 1916, **29**, 457—458).—Ten c.c. of the urine are diluted with three volumes of water and the solution divided into two parts. To the one three drops of 1% permanganate are added, when, in presence of bilirubin, decolorisation occurs owing to its oxidation to a colourless substance, and the liquid appears as if it had been largely diluted with water. Should the urine contain urochromogen, which gives an intense yellow colour with permanganate, 25 c.c. are first shaken with 20 grams of ammonium sulphate and filtered. The residue containing the bilirubin is washed with ammonium sulphate solution and dissolved in slightly alkaline water, the solution is neutralised with acetic acid, and tested as above. A second colouring matter which disturbs the bilirubin test is urobilinogen, which by oxidation is converted into the brown urobilin. In this case either the acidified urine may be extracted with ether, or on proceeding as when urochromogen is present, the colouring matter remains on the filter as urobilin, which has no disturbing influence on the bilirubin test. G. F. M.

Blood-Serum. I. Estimation of Non-colloidal Nitrogen. WILLIAM H. WELKER and FREDERICK H. FALLS (*J. Biol. Chem.*, 1916, **25**, 567—570).—Five c.c. of serum are measured into a 250 c.c. volumetric flask, 75 c.c. of alumina cream are added, and mixed by shaking. The mixture is diluted to the mark with water and the contents of the flask again mixed and filtered. The total nitrogen is estimated in 125 c.c. of the filtrate by Kjeldahl's method.

The authors find by experiment that not all the non-colloidal nitrogen is estimated by this method, although the results tally well with those obtained by the Folin and Denis method (A., 1912, ii, 703). H. W. B.

Significance of Colour Changes in Oxydase Reagents. G. B. REED (*Bot. Gaz.*, 1916, **61**, 430—432).—The amount of oxidation required to produce colour in ordinary oxydase reagents, or in plant chromogens, is very small; oxidation may, however, continue without necessarily producing further change in colour.

The amount of oxidation necessary to produce colour in the different reagents varies considerably; and these reagents may be calibrated so that the effects of the oxidation may be measured, and the oxidation necessary to produce a change of colour in presence of oxydases expressed in grams of oxygen.

N. H. J. M.

General and Physical Chemistry.

Birefractive Colloidal Solutions. W. Reinders (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 189—197).—It has been shown that colloidal solutions of vanadium pentoxide are under certain conditions birefringent and resemble crystalline liquids in their general behaviour (compare Diesselhorst and Freundlich, this vol., ii, 65; Kruyt, *ibid.*, 486). Whether the colloidal particles are themselves anisotropic or whether the anisotropy is due to differences in the elastic properties of the solution in different directions has not been settled, and the experiments now described were directed to the solution of this question.

These experiments show that freshly prepared colloidal solutions of vanadium pentoxide are not birefringent; on keeping the solutions they slowly develop double refraction, and this is apparently due to the formation and increase in size of ultra-microscopic, crystalline needles.

By modifying suitably the conditions of formation of slightly soluble substances, which ordinarily form microscopic crystals, so as to obtain these in the form of sols, it has been found possible to prepare colloidal solutions which exhibit double refraction analogous to that of vanadium pentoxide sols. Successful results were obtained with mercurous chloride and lead iodide, and it would therefore seem that the colloidal particles of vanadium pentoxide are in reality micro-crystalline. H. M. D.

Spectroscopic Control of Material Used in Atomic Weight Determinations. A. de Gramont (*J. Chim. Phys.*, 1916, **14**, 336—339).—The author, in advocating the spectroscopic examination of all material used in atomic weight determinations, gives a list of the impurities found in some forty-two elements and their salts. These substances have been regarded as pure, but in some cases spectroscopic analysis reveals the presence of as many as eight or nine other elements. Thus in the case of silver, the elements calcium, copper, gold, magnesium, and iron are always present, whilst mercury, lead, and bismuth are generally present.

J. F. S.

The High-frequency Spectra (L-Series) of the Elements Lutecium–Zinc. Einar Friman (*Phil. Mag.*, 1916, [vi], **32**, 497—499. Compare this vol., ii, 277, 362, 405).—Wave-length measurements are recorded for lines in the *X*-ray spectra of the elements ranging from zinc (atomic number = 30) to lutecium (atomic number = 71). For certain groups (α_2, α_1, and β_2) the graph obtained by plotting the square-root of the frequency against the atomic number is a straight line, but other groups yield curves slightly convex to the atomic number axis. H. M. D.

Emission and Absorption in the Infra-red Spectrum of Mercury. RAYMOND C. DEARLE (*Proc. Roy. Soc.*, 1916, [*A*], **92**, 608—620).—The relative intensities of infra-red lines in the spectrum emitted by the mercury arc have been examined under conditions in which the energy consumption of the arc was varied.

In the case of the three lines $\lambda = 1{\cdot}014\ \mu$, $1{\cdot}357\ \mu$, and $0{\cdot}6717\ \mu$, which are the first three members of the series $\nu = (2{\cdot}5, S) - (m, P)$ corresponding respectively with $m = 2$, 3, and 4, it is found that the curves, which are obtained by plotting the intensities against the wave-lengths, resemble closely the ordinary energy curves, in that increased energy consumption is accompanied by an increase in the intensity of the lines, the relative magnitude of which increases with diminution in the wave-length. A comparison of the two lines $\lambda = 1{\cdot}014\ \mu$ and $\lambda = 0{\cdot}5461\ \mu$, which belong to different series, has shown, on the other hand, that increased consumption of energy by the arc causes a relatively greater increase in the intensity of the line of greater wave-length.

Examination of the absorption spectrum between $\lambda = 1{\cdot}00\ \mu$ and $\lambda = 1{\cdot}20\ \mu$ has afforded evidence of absorption at every wave-length for which there is a line of emission in the mercury arc spectrum. Strong absorption occurs at $\lambda = 1{\cdot}014\ \mu$, $\lambda = 1{\cdot}129\ \mu$, and $\lambda = 1{\cdot}20\ \mu$, the absorption at the first and last wave-lengths being clearly marked even at very low vapour pressures. The two lines in question are the first members of the series $\nu = (2{\cdot}5, S) - (m, P)$ and $\nu = (1{\cdot}5, s) - (m, P)$ respectively. H. M. D.

The Bunsen Flame Spectra of Metallic Vapours. J. C. MCLENNAN and ANDREW THOMSON (*Proc. Roy. Soc.*, 1916, [*A*], **92**, 584—590).—Investigation of the spectra emitted by Bunsen flames supplied with the vapours of various metals, has shown that the fundamental frequencies are given by mercury, cadmium, and magnesium, but not by zinc. The mercury line $\lambda = 2536{\cdot}72$ was strongly developed. In the case of cadmium, a gently burning flame showed the characteristic line $\lambda = 3260{\cdot}17$, whilst a flame burning vigorously gave in addition $\lambda = 2288{\cdot}79$, although this was only faintly developed on the spectrograms. The magnesium flame gave the line $\lambda = 2852{\cdot}22$ faintly but clearly.

These observations confirm the view that the fundamental frequency for mercury and cadmium corresponds with $\nu = (1{\cdot}5, S) - (2, p_2)$, whilst that for magnesium is given by $\nu = (1{\cdot}5, S) - (2, P)$. The line $\lambda = 2288{\cdot}79$ shown by a strongly burning cadmium flame also belongs to the series represented by the latter formula.

The results obtained with thallium give no indication of the fundamental frequency lines in the Bunsen flame spectrum. The lines exhibited are $\lambda = 5350{\cdot}65$ and $\lambda = 3775{\cdot}87$, and these appear to be analogous to the doublet yellow lines in the sodium spectrum. From this it is evident that the behaviour of thallium vapour in a Bunsen flame is exactly similar to that of sodium. H. M. D.

The Ionisation of Metallic Vapours in Flames. J. C. MCLENNAN and DAVID A. KEYS (*Proc. Roy. Soc.*, 1916, [*A*], **92**, 591—608).—The electrical conductivity of flames supplied with the

vapours of various metals has been examined with the view of ascertaining the existence of relations between the ionisation of the metal and its spectral behaviour (compare preceding abstract). The results obtained show that mercury and magnesium, the spectra of which consist of single lines of fundamental frequency, are both ionised to an appreciable extent. Zinc vapour, which gives no characteristic lines, is, on the other hand, non-ionised. Cadmium vapour is also non-ionised, although its spectrum shows the fundamental line $\lambda=3260{\cdot}17$ when the flame is weak and $\lambda=2288{\cdot}79$ in addition when the flame is burning strongly. The conductivity of thallium flames is relatively very large, although the emitted light is not of fundamental frequency.

The results are discussed in reference to Bohr's theory, but the authors arrive at the conclusion that the differences in the behaviour of the various metals are such that no definite argument in favour of or against this theory can be put forward on the basis of the observations. H. M. D.

The Ionisation Potentials of Magnesium and other Metals and their Absorption Spectra. J. C. McLennan (*Proc. Roy. Soc.*, 1916, [*A*], **92**, 574—583).—Previous experiments have shown that the single line $\lambda=2832{\cdot}22$ is emitted by magnesium vapour when bombarded by electrons the energy of which exceeds that acquired in a fall of potential of approximately 4·5 volts. The absorption spectrum of non-luminous magnesium vapour consists of narrow, sharp bands at $\lambda=2852{\cdot}22$ and $\lambda=2026{\cdot}46$, which are the first two members of the single series represented by the formula $\nu=(1{\cdot}5, S)-(m, P)$. The simplest Bunsen flame spectrum of magnesium also consists of the single line $\lambda=2852{\cdot}22$, and since the vapour in the flame is ionised, it would seem that the ionising potential is deducible from the quantum relation $Ve=h\nu$, which yields the value of 4·28 volts.

Whilst the frequency of the lines in the single line spectrum of zinc, cadmium, and mercury is given by $\nu=(1{\cdot}5, S)-(2, p_2)$, no evidence of the corresponding magnesium line has been obtained in either bombardment or absorption experiments. The behaviour of magnesium resembles, however, that of calcium, strontium, and barium in that the single-line spectra correspond with $\nu=(1{\cdot}5, S)-(2, P)$, from which the ionising potentials can be calculated by the use of the quantum theory.

Experiments with thallium vapour afford no evidence of lines corresponding with either of the above series. The absorption spectrum of the vapour at low densities consists of a sharp band at $\lambda=3775{\cdot}87$ and at higher densities of this band together with diffuse bands at $\lambda=3230$ and $\lambda=3000$. H. M. D.

Ethyl Succinylsuccinate. II. A Study of the Absorption Spectra of some Derivatives. Harvey C. Brill (*Philippine J. Sci.*, 1916, **11**, [*A*], 59—71. Compare A., 1915, i, 648).—The absorption spectra of the following compounds related to, or derived from, ethyl succinylsuccinate were studied: Ethyl *p*-dihydroxytere-

phthalate in alcohol, and in presence of 2 mols. of sodium ethoxide; ethyl *p*-diaminoterephthalate in alcohol, and in presence of hydrochloric acid; methyl $\Delta^{1:4}$-dihydroterephthalate, and ethyl terephthalate; *cyclo*hexanedione in alcohol; chloranil in acetic acid; *p*-dihydroxybenzoquinone and its potassium salt; and *p*-dichlorodiethoxybenzoquinone. The dihydroxyterephthalate gives very similar absorption bands to the succinylsuccinate, and both were found to be about 90% enol. The spectra of both the dihydroterephthalate and *cyclo*hexanedione show selective absorption, thus affording further evidence of the correctness of the theory that selective absorption is intimately associated with the partial valency equilibrium of the compound. Hartley had only observed general absorption with *cyclo*hexanedione (T., 1898, **73**, 598). Evidence was obtained that in alcoholic solution this substance exists only in the keto-form, and that *p*-dihydroxybenzoquinone is keto-enolic.

G. F. M.

Temperature-coefficients of the Action of Monochromatic Light on Chlorine–Hydrogen Mixtures. M. PADOA (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 215—218).—The measurements were made by determining the contraction in volume of the mixed gases by means of an apparatus similar to that used by Bunsen and Roscoe, the temperatures used being 10°, 20°, 30°, and 40°. The temperature-coefficients were found to be: white light, 1·29; green ($\lambda=550$—$530\mu\mu$), 1·50; blue ($\lambda=490$—470), 1·31; violet ($\lambda=460$—440), 1·21; ultra-violet ($\lambda=400$—350), 1·17. T. H. P.

Temperature-coefficients of the Action of Monochromatic Light on Photographic Plates and Papers. M. PADOA and L. MERVINI (*Atti R. Accad. Lincei*, 1916, [v], **25**, ii, 168—171).—The authors have exposed a photographic plate under a negative at 15° and at −85° to the action of the following lights: red, λ 650—620 $\mu\mu$; yellow, 620—585; green, 550—530; violet, 437—394 and white, the plates used with yellow and green light being sensitised with ammonia, silver nitrate, and erythrosin, and those used with red light with aqueous-alcoholic pinachrome solution. The exposures were adjusted so that in all cases positives of equal intensity were obtained on development with one and the same developer for equal periods of time. With each light the temperature-coefficient of the action of light on the plate is 1·05. The direct blackening of so-called citrate paper by white, blue (λ 470—490), and ultra-violet light (λ 400—350) at 15° and −85° was also investigated, the corresponding temperature-coefficients being 1·16, 1·19, and 1·07 respectively. The varying behaviour with the plates and papers seems to indicate that the formation of a latent image on the plate is not due to a photochemical process consisting in the decomposition of silver chloride into its elements.

T. H. P.

A Photochemical Decomposition of some Acid Chlorides. S. C. J. OLIVIER (*Rec. trav. chim.*, 1916, **36**, 117—125).—An examination of the behaviour of certain acid chlorides when exposed in

solution in different solvents to the action of sunlight or the light from a mercury lamp. Of the acid chlorides examined, decomposition was only clearly established in the case of benzenesulphonyl chloride or its derivatives, and then only when in solution in ether or chloroform. In the case of *p*-chlorobenzenesulphonyl chloride, the products of decomposition in open vessels were: chlorine, hydrogen chloride, *p*-chlorobenzenesulphonic acid, and some aldehyde arising from the decomposition of the combination of the ether with the chlorine. The decomposition is brought about by the combined action of the oxygen in the air and the light. The presence of water in the ether is without any influence on the photolysis. The decomposition is far greater in ethereal solution than in chloroform solution, and is much greater in concentrated than in dilute ethereal solution. The acid chlorides examined, arranged in descending order of ease of decomposition, are: *p*-chlorobenzenesulphonyl chloride, *m*-nitrobenzenesulphonyl chloride, benzenesulphonyl chloride, and *p*-toluenesulphonyl chloride, whilst acetyl chloride, chloroacetyl chloride, and benzoyl chloride showed no signs of decomposition. W. G.

Radio-elements. O. Hönigschmid (*Ber.*, 1916, **49**, 1835—1865).—A lecture delivered before the German Chemical Society on June 3rd, 1916. The bearing of recent work on chemical theory is discussed. J. C. W.

Results of Crystal Analysis. III. L. Vegard (*Phil. Mag.*, 1916, [vi], **32**, 505—518. Compare this vol., ii, 405).—The crystalline structure of xenotime (YPO_4) and of anatase (TiO_2) has been examined by means of the *X*-ray spectrometer.

In its crystalline form and physical properties, xenotime is very similar to zircon ($ZrSiO_4$). Both belong to the ditetragonal bipyramidal class, and the axial ratios are very nearly the same. The valency differences suggest, however, a difference of structure, and the *X*-ray observations show, in fact, that the lattice of xenotime is not of the zircon type, the difference being due to a different spacing of the oxygen atoms. In xenotime these are arranged in groups of four round each atom of phosphorus, whilst in zircon the atoms of zirconium and silicon are similarly spaced with reference to the oxygen atoms. This difference may be expressed by the constitutional formulæ YPO_4 and ZrO_2,SiO_2. At the same time the lattice systems are such that the crystallographic similarity is readily accounted for.

The observations on anatase suggest that the lattice is of the diamond type drawn out in the direction of the tetragonal axis. In the case of rutile there appear to be two lattices of the diamond type put inside one another in such a way that the elementary cell is not altered. The difference may be expressed by the formulæ TiO_2 for anatase and $(TiO_2)_2$ for rutile.

When the dimensions of the lattices of the zircon group of minerals are compared it is found that there is a small but regular increase as the atomic number of the central atom increases. The

distance between the central atom and the associated oxygen atoms also increases with the atomic number of the central atom, and this corresponds with a diminishing affinity for oxygen. H. M. D.

A Critical Test of the Crystallographic Law of Valency Volumes. The Crystalline Structure of the Alkali Sulphates. A. OGG and F. LLOYD HOPWOOD (*Phil. Mag.*, 1916, [vi], **32**, 518—525).—The crystalline structure of the isomorphous sulphates of potassium, rubidium, ammonium, and cæsium has been examined by means of the *X*-ray spectrometer. The observations show that the elementary cell or unit rhomb of each of these crystals contains four molecules. Although the complete structure has not been elucidated, it seems probable that the sulphur atoms are located at the corners and centres of the faces of the cell, an arrangement which would give a pseudo-hexagonal structure for the sulphur atoms in planes parallel to the (001) face. The space arrangement of the metallic atoms is also said to be hexagonal.

By comparison of the volumes of the elementary cells it is found that those for ammonium and rubidium sulphate agree very closely. The replacement in the elementary cell of eight atoms of rubidium by eight atoms of nitrogen and thirty-two atoms of hydrogen is therefore unaccompanied by any appreciable change of volume. This is regarded as conclusive evidence against the general truth of the law of valency volumes and the theory that crystal structure is determined by the closest packing of the constituent atoms or their spheres of influence. H. M. D.

Apparatus for the Measurement of Electric Resistance of Material in the Solid State at High Temperatures. P. SALDAU (*Iron Steel Inst. Carnegie Scholarship Mem.*, 1916, **7**, 195—231).—The rods of metal to be examined are heated in an electric furnace in an atmosphere of coal gas, freed from oxygen by passing through an alkaline pyrogallol solution. The rods are supported by rods of chrome-nickel steel. A Kelvin double bridge method of measurement is used.

In the iron–carbon system the electrical method has allowed the curves of allotropic change and of the solubility of cementite to be determined with accuracy. The line of transformation of γ- into β-iron is of a new form, with a break at 900° and 0·02% C, but the transformation of γ- into α-iron and the line of solubility of cementite in γ-iron are straight. A new horizontal boundary line in the austenite region is also found at 980°, unaccompanied by any thermal change. The change of resistance of steel with carbon percentage is not represented by a straight line. The eutectoid steel has a higher resistance throughout the range of the transformation than steel on either side of the eutectoid point. Further experiments in nitrogen indicate that the Ar_3 point for pure iron lies above 910°. C. H. D.

The Size and Mobility of the Carriers of Electricity in Liquids. II. G. VON HEVESY (*Jahrb. Radioaktiv. Elektronik*, 1916, **13**, 271—296).—In a previous paper (*ibid.*, 1914, **11**, 419) it was

suggested that the nature of the ions in a solution is determined by the size of the ionic nucleus and the magnitude of the electric charge. If the ratio of the charge to the volume of the ion is greater than a certain normal value, which for aqueous solutions at 18° corresponds with a mobility of about 60, the nucleus tends to combine with the solvent until this normal value is reached.

In connexion with this view, measurements have been made of the mobilities of isomeric ions carrying different charges, giving for the mobilities at 18° the following numbers: $Fe^{\cdot\cdot}$, 48; $Fe^{\cdot\cdot\cdot}$, 45; FeC_6N_6''', 75; FeC_6N_6'''', 72; MnO_4', 50; MnO_4'', 68. These results show that the mobility is not proportional to the charge in the ion, and the relations between the pairs of values are considered to support the above hypothesis.

When the ionic size exceeds the normal value, as it does for most organic ions, there is no tendency for the ion to combine with the solvent.

In the case of highly ionised molten salts the tendency to form complex ions by combination with the solvent is restricted by the relatively small proportion of non-ionised molecules present, and free ions are to be expected under these conditions. The fact that the $Pb^{\cdot\cdot}$ ion has a much greater mobility in fused lead chloride than in water under comparable conditions is consistent with this view. That the contraction which accompanies the formation of aqueous solutions of multivalent electrolytes is greater than the volume charge for univalent electrolytes is also considered to support the author's theory. H. M. D.

The Influence of Boric Acid on the Conductivity of some Dibasic Acids. J. Böeseken and P. E. Verkade (*Rec. trav. chim.*, 1916, **36**, 167—179).—The authors have examined the influence of boric acid on the electrical conductivity of solutions of oxalic, malonic, succinic, glutaric, adipic, maleic, fumaric, and glutaconic acids. In the case of oxalic acid, which may be considered as an α-hydroxy- or α-ketonic acid, there is a marked increase in the conductivity. This acid thus resembles pyruvic acid in its behaviour (compare this vol., ii, 73, 209), and gives a combination with the boric acid. Malonic acid shows a slight diminution in conductivity, the diminution being practically zero, and it is very probable that this acid forms a complex combination with boric acid. All the other acids showed a diminution in conductivity amounting to 7—13% at a concentration $M/24$, and 9—22% at a concentration $M/192$, the diminution appearing to bear some relation to the dissociation constant of the acid. Finally, the authors point out that, with the exception of maleic acid, all those acids which show an increase in conductivity indicative of the formation of complexes with boric acid also exert a dissolving and reducing action on manganese dioxide, whilst the acids which show a diminution in conductivity have no action on manganese dioxide (compare Söhngen, *Rec. trav. chim.*, 1915, **35**, 216).

W. G.

Recognition of Complexes in Solution by the Electrical Conductivity Method. C. SANDONNINI (*Gazzetta*, 1916, **46**, ii, 205—219. Compare A., 1915, ii, 406, 668).—The conductivities at 25° of mixtures in different proportions of various pairs of salts have been measured.

As a type of mixtures of solutions of salts which do not combine and have nearly equal degrees of dissociation, sodium and potassium chlorides at equivalent concentrations were chosen. The conductivities agree very closely with those calculated according to the law of mixtures. Similar measurements with mixtures of sodium chloride and sulphate show marked differences between the calculated and observed conductivities, the maximum divergence, 2·2%, corresponding with the mixture containing equal numbers of equivalents of the two salts; in this case the latter are dissociated to very different extents.

The following mixtures, which form complexes, were also examined: $KCl-HgCl_2$, $NaCl-HgCl_2$, and $KCl-CdCl_2$; the conductivity curves are smooth, but diverge appreciably from straight lines. It is evident that the absence of an elbow in such a curve cannot be regarded as a sign that no complex is formed, since in these three cases complexes exist in solution, but in a condition of partial dissociation into their components. Vojtaschevski's view (A., 1913, ii, 1015) that Costăchescu and Apostoi's results (A., 1912, ii, 528) are due to experimental errors is confirmed.

T. H. P.

Effect of Neutral Salts on the Dissociation Constant of Water. I. M. KOLTHOFF (*Chem. Weekblad*, 1916, **13**, 1150—1156). —Measurements of the dissociation constant of water at 18° have demonstrated that the mercury oxide electrode gives good results for the concentration of the hydroxyl ions, especially when P_{OH} approximates to 7; but in presence of chlorides this electrode is not satisfactory. For alkaline liquids containing nitrate the hydrogen electrode is unsuitable for the determination of P_H. The presence of small quantities of salts, up to about normal concentration, has no appreciable influence on the dissociation constant of water. The action of salts on indicators is probably due to an increase in the dissociation constant of the indicators. A. J. W.

Influence of the Potassium Ion and of the Calcium Ion on the Ferri-Ferro-Cyanide Potential. EUGENE P. SCHOCH and WILLIAM A. FELSING (*J. Amer. Chem. Soc.*, 1916, **38**, 1928—1947). —Series of electrical conductivity measurements have been made at 25° with solutions of potassium ferrocyanide, potassium ferricyanide, and with mixtures of these salts with one another and with potassium chloride; also with calcium ferrocyanide, calcium ferricyanide, and with mixtures of these salts with one another and with calcium chloride. The results were compared with values calculated on the assumption that the law of mixtures is true, whence it is shown that a fairly good agreement is obtained. The electro-potential of the whole of the above-mentioned mixtures

were measured at 25° against a normal calomel electrode. The concentration of the constituent ions and the non-ionised molecules in these mixtures was calculated on the assumption that intermediate ions are absent. The following empirical formulæ were deduced to represent the dependence of the potentials on the concentration of the constituents of the solution over a range of concentration of potassium or calcium ion from 10 to 400 milli-equivalents per litre:

$E_{obs.} = 0{\cdot}554 + 0{\cdot}0591 \log[Fe(CN)_6{}^{III}]\cdot(K^{\cdot})^{0\cdot75}/[Fe(CN)_6{}^{IV}]$;
$E_{obs.} = 0{\cdot}0753 + 0{\cdot}0591 \log[K_3Fe(CN_6)]\cdot(K^{\cdot})^{0\cdot675}/[K_4Fe(CN)_6]$;
$E_{obs.} = 0{\cdot}0916 + 0{\cdot}0591 \log[Fe(CN_6)^{III}]\cdot(Ca^{\cdot\cdot})^{0\cdot625}/[Fe(CN)_6{}^{IV}]$; and
$E_{obs.} = 0{\cdot}1415 + 0{\cdot}0591 \log\cdot[Ca_3(FeC_6N_6)_2]\cdot(Ca^{\cdot\cdot})^{0\cdot575}/[Ca_2Fe(CN)_6]$.

A new method is described for deriving the significant values of n and k for such salts as the ferrocyanides and ferricyanides, which have values that vary widely with changes in concentration. It is shown that the n values of the two potassium salts change equally with Σi. The same is true for the calcium salts. It is found that the maximum values of n (that is, the limits they approach with decreasing Σi) bear a simple numerical relationship to the indices of the potassium or calcium ions in the potential formulæ given above. It is shown also that certain of the observed relationships are necessary consequences of the assumption that the concentration activity relation of each component in the conductivity functions is the same as in the potential function.

J. F. S.

Application of the Theory of Allotropy to Electromotive Equilibria. V. A. SMITS and A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 133—148. Compare this vol., ii, 410).—The views put forward in the previous paper have been extended to the consideration of electromotive equilibria in which the metal concerned yields multivalent ions, and to the more complex case in which the metal forms two kinds of ions differing in valency. The theory is discussed in reference to the potential difference at the surface of contact of a metal and a liquid, and also to the phenomena of polarisation and passivity. H. M. D.

The Hydrogen and Chlorine Ion Activities of Solutions of Potossium Chloride in 0·1 Molecular Hydrochloric Acid. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1916, **38**, 1986—1995). —A series of electromotive force determinations has been made at 25° of cells of the types $H_2|KCl(c)$ in $HCl(0{\cdot}1N)HgCl|Hg$ and $Hg|HgCl,KCl(c)+KCl(0{\cdot}1N)|KCl(0{\cdot}1N)HgCl|Hg$, in which c is the concentration of potassium chloride. This was varied from $0{\cdot}060N$ to $3{\cdot}000N$. From the values of the *E.M.F.* obtained, the *E.M.F.* of cells of the type $H_2|KCl(c)$ in $HCl(0{\cdot}1N)|HCl(0{\cdot}1N)H_2$ can be calculated if the ion activities of $0{\cdot}1N$-potassium chloride and $0{\cdot}1N$-hydrochloric acid are known. The values obtained in the present paper, as well as those previously published (this vol.,

ii, 8), indicate that if the ion activity of 0·1*N*-potassium chloride is 0·0730, then the ion activity of 0·1*N*-hydrochloric acid is 0·0755. From these two values and the *E.M.F.* measurements of the above-mentioned cells, the hydrogen and chlorine ion activities of solutions of potassium chloride (0—3·0*N*) in 0·1*N*-hydrochloric acid have been calculated. An accuracy of about 1·0% is claimed for the results. J. F. S.

Electrolytic Reduction of Sulphuric Acid in Alcoholic Solution and Stability of Ethyl Alcohol towards Cathodic Hydrogen. U. Pomilio (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1915, [iii], **21**, 19—27. Compare A., 1915, i, 937).—Dilute solutions of sulphuric acid in alcohol are reduced by electrolytic hydrogen liberated from a nickel or lead cathode, sulphur and hydrogen sulphide occurring among the products of the reduction. On the other hand, ethyl alcohol acidified with hydrochloric acid is not appreciably attacked by cathodic hydrogen under widely varied conditions. T. H. P.

Overvoltage Tables. I. Cathodic Overvoltages. Edgar Newbery (T., 1916, **109**, 1051—1066).—The overvoltages shown by various electrode materials when used as cathodes in *N*-sulphuric acid and *N*-sodium hydroxide have been measured with the object of supplying data which may serve to indicate the conditions for obtaining suitable overvoltages and maintaining these constant where this is possible. The recorded data show the influence of current density and also of time on the overvoltage, the magnitude of which is of essential importance in the investigation of electrolytic reductions. H. M. D.

Overvoltage Tables. II. Anodic Overvoltages. Edgar Newbery (T., 1916, **109**, 1066—1078).—The overvoltages of various anodes in *N*-sulphuric acid and *N*-sodium hydroxide have been measured by the method employed in the determination of cathodic overvoltages. The tabulated results show that anodic overvoltages are in general much higher than cathodic, none of the electrodes examined giving an overvoltage of less than 0·4 volt. For this reason, electrolytic oxidation tends to give highly oxidised products or to destroy the substance, with formation of carbon dioxide. For moderated oxidations, gas carbon at low current densities would seem to be the most suitable anode, although its overvoltage increases slowly with time. Iridium anodes are also suitable for acid electrolytes, the overvoltage being relatively low (0·5 volt in *N*-sulphuric acid) and constant.

For general work, lead is the most suitable anode for dilute sulphuric acid or sulphate solutions, graphite for chloride solutions, and pure nickel or nickel steel containing a large proportion of nickel for alkali solutions or fusions. H. M. D.

Chemical Reactions under the Influence of the Electric Discharge in an Atmosphere of an Inert Gas. Franz Skaupy (*Ber.*, 1916, **49**, 2005—2006).—The author has recently found that

the passage of a direct current discharge through a mixture of gases effects a separation which is controlled by the magnitude of the ionisation potentials of the components. A chemical compound in the state of vapour is usually extensively dissociated under the influence of the discharge, and it might therefore be possible to separate the dissociation products, in the light of the above. This can be realised if the discharge is carried by an inert gas (helium gives the greatest potential fall; argon can be used for low potential work and at high pressures), and especially if by some condensation or absorption device the electrodes are protected from the dissociation products. Thus, if aluminium chloride vapour is led into the middle of such a discharge tube, aluminium wanders towards the cathode and may be condensed in a widened part of the tube.

The use of an inert gas to carry the current may also be of service in connexion with other applications of the discharge, either direct or alternating. Thus hydrocarbons may be polymerised without the charring that usually occurs when ordinary, heated electrodes are used. The polymerides condense in the cold parts of the tube as transparent, yellowish-brown oils. Mixtures of gaseous carbon compounds and nitrogen yield organic nitrogen compounds. J. C. W.

Relation between Paramagnetism of Compounds and the Form of Combination. A. QUARTAROLI (*Gazzetta*, 1916, **46**, ii, 219—234. Compare this vol., ii, 290).—The author has applied Pascal's method (A., 1910, ii, 483) to the measurement of the magnetic susceptibility of ferric and ferrous, cobaltous and cobaltic, nickelous and nickelic, and manganous hydroxides, and of ferrites obtained, for example, by precipitation of ferric chloride solution with ammonia solution in presence of magnesia mixture; similar measurements of chromic sulphate and potassium and sodium chromites were made by Quincke's method.

The exception to the general rule shown by ferrous and ferric salts is upheld by the hydroxides, ferrous having a less susceptibility than ferric hydroxide; the other pairs of hydroxides examined conform to the rule. The occurrence of the magnetic metal in an acid residue or anion does not annul or even appreciably reduce the susceptibility, which is, indeed, increased in some cases. The low magnetic properties of chromates, permanganates, manganates, etc., are occasioned by the high valencies of the magnetic metal in these compounds.

The significance of these results is discussed, especially in relation to the mode of interpretation of the doubled formulæ of certain salts. In such compounds, one of the two atoms of the metal is more loosely bound than the other, this phenomenon being particularly evident with mercurous chloride and oxide and cuprous chloride. Further, it has been shown by Feytis that the more labile the combination of two substances the more nearly will the molecular susceptibility of the compound approach to the sum of the susceptibilities of the components. From this it is evident

why ferric chloride is more, and cuprous chloride less susceptible than would be indicated by the general rule, iron being far more magnetic than its compounds, whereas copper is diamagnetic and its normal (cupric) salts magnetic. These views are supported by the results of an investigation of the magnetic properties of the so-called ferroso-ferric saline hydroxides. Unlike other saline hydroxides, these compounds have not magnetic constants intermediate to those of the two hydroxides, as would be the case with molecular compounds or mixtures of the two; the constants are, indeed, extremely high and almost of the same order of magnitude as that of metallic iron. Such compounds constitute, therefore, special types, part of the iron atoms present maintaining their individuality almost unaltered; in the author's opinion, the iron exists in the same condition as the oxygen in peroxides, and the analogous name of *permetallic hydroxides* is suggested. T. H. P.

Combined Expansibility Product. L. GAY (*J. Chim. Phys.*, 1916, **14**, 291—327).—A mathematical paper in which the combined expansibility product [le self-produit d'expansibilité] is considered. This quantity is defined for the case of a mixture of two liquids as $W = \pi_A^a . \pi_B^\beta$, in which π_A and π_B are the expansion pressures respectively of A and B, and a and β are the numbers of gram-molecules of A and B present in the mixture. Among other relationships, those of the thermodynamic potential are considered. The application of this function with the phase rule and the law of mass action is also considered mathematically. J. F. S.

Deductions from the Eötvös-Ramsay Law. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1916, **14**, 285—290).—A mathematical paper in which the author, starting from the Eötvös–Ramsay rule, $\gamma V^{2/3} = a(c-t)$, deduces the two equations

$$\gamma V^{2/3} = a(t_c - t)(1 - 1/m - nt)$$

and $\gamma = a'(t_c - t)(1 - 1/m' - n't)$, in which m, m', n, and n' are constants. Further, since $V = M/d$, in which M is the molecular weight and d the density, he is able to calculate the density of liquids over a considerable range of temperature from the surface tension. It is found that the maximum density of a liquid is given by the formula $d_m{}^{2/3} = a'/a . M^{2/3}$. For the substances benzene, chlorobenzene, carbon tetrachloride, ether, methyl formate, and ethyl acetate the maximum density is shown to be identical with the density at the point of solidification. J. F. S.

Relation of Molecular Cohesion to Surface Tension and Gravitation; with a Method of Determining "a" of van der Waals' Equation without Assumptions; and the Explanation of the Meaning of the Constants in the Surface Tension Law of Eötvös, and the Latent Heat Formulæ of Dieterici and Mills. A. P. MATTHEWS (*J. Physical Chem.*, 1916, **20**, 554—596. Compare A., 1913, ii, 929).—A theoretical paper in which the author revises and extends a number of his considerations in connexion

with molecular cohesion. The main points considered in the paper are: (1) A method of evaluating the constant "a" of van der Waals's equation from the internal latent heat of vaporisation. (2) The proof that the values of "a" thus obtained are equal to the two-thirds power of the product of the molecular weight and the number of valencies in the molecule. (3) The cohesive attraction of two molecules at unit distance is shown to be equal to the two-thirds power of their gravitational attraction at this distance multiplied by the two-thirds power of the ratio of the number of valencies to the molecular weight, or if M^2K, which is "a" for a single pair of molecules, is the cohesional attraction at unit distance, and m^2k the gravitational attraction of the same molecules at the same distance, then the relation $M^2K=(m^2k \times \text{number of valencies/molecular weight})^{2/3}$; (4) a discussion of the meaning of the above relationship between cohesional and gravitational attraction. (5) The theoretical derivation of the relationship between cohesion and surface tension, and the derivation of the Eötvös surface tension law, $SV_1^{2/3}=C(T_c-T)$. In this connexion, the real significance of the constant C is pointed out, and the reason for its variation with different substances. (6) An expression to show the number of layers in the surface film is deduced. This has the form $n=T_c/(T_c-T)^{2/3}$. (7) The relationship $[T_c/(T_c-T)]^{1/3}=d_0/(d_1-d_v)$ is partly derived. (8) A meaning is attributed to the constant C' in Dieterici's expression of the relationship between the internal latent heat of vaporisation, $L-E$, and the work done in expanding from the density of the liquid to that of the vapour, that is, $L-E=C'RT\log_e d_1/d_v$; and (9) a meaning is attributed to the constant μ', in Mills's expression of the relationship of the internal latent heat to the difference between the cube roots of the density of liquid and vapour, that is, $L-E=\mu'(d_1^{1/3}-d_v^{1/3})$.

J. F. S.

Surface Tension Effects in the Intercrystalline Cement in Metals and the Elastic Limit. F. C. THOMPSON (*J. Iron Steel Inst.*, 1916, **93**, 155—210).—The mechanical properties of metals may be explained in large part by the surface tension effects occurring in the thin, intercrystalline layer. The thickness of the film d may be estimated in some cases by means of the relation $E=2T/d$, where E is the elastic limit and T the surface tension of the amorphous material. The value of T may be calculated approximately if the surface tension in the liquid state and the densities in both the liquid and solid states at known temperatures are known. The diminution of tensile strength of a pure metal may be accounted for qualitatively on the same assumption.

The theoretical explanation may be extended to carbon and alloy steels, and accounts for the variation of the elastic limit with composition and with fineness of grain. The hardness of a metal is chiefly dependent on the composition of the crystalline portion, whilst the elastic limit depends rather on the nature and distribution of the intercrystalline cement.

C. H. D.

The Viscosity and Hydration of Colloidal Solutions. EMIL HATSCHEK (*Biochem. J.*, 1916, **10**, 326—330).—Arrhenius has recently applied his formula, $\log \eta = \theta C$, where η = viscosity, C = molecular concentration, and θ is a constant, to the investigations of Chick (A., 1914, ii, 625) on the viscosity of pure solutions of proteins. For this purpose, Arrhenius considers that C can be expressed by the equation $C = 100p/100 - (n+1)p$, where p = number of grams of solute in 100 grams of solution and n = number of grams of solvent associated with each single gram of solute. From these equations, $\log \eta = \theta . 100p/100 - (n+1)p$. This equation has been found to fit Chick's results with the proteins. The author shows, however, that this formula of Arrhenius does not apply to sols in organic solvents, for in some cases the association factor (n) is found to be negative. He draws the conclusion that Arrhenius's equation is a purely analytical interpolation formula in which the factors cannot have the analytical meaning assigned to them. S. B. S.

Abnormal Adsorption by Filter Paper. RUBY RIVERS MURRAY (*J. Physical Chem.*, 1916, **20**, 621—624).—A number of experiments on the adsorption of hydrochloric acid by filter paper made by Evans (A., 1906, ii, 429) have been repeated. It is shown that the adsorption of hydrochloric acid by filter paper increases with increasing concentration within the range examined ($0·216N$—$0·986N$). When filter paper is kept in contact with hydrochloric acid solutions for seven to ten days, a change occurs in the paper which decreases the adsorption to less than one-half its original value. It is shown that the abnormal results obtained by Evans (*loc. cit.*) with hydrochloric acid are due to analytical errors.
J. F. S.

Diffusion in Solutions. J. D. R. SCHEFFER and F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch, Amsterdam*, 1916, **19**, 148—162).—According to Einstein (*Ann. Physik*, 1906, [iv], **19**, 289, 371), the relation between the rate of diffusion of a substance and the size of the particles is given by the equation $D = RT/N6\pi a\eta$, in which D is the diffusion constant, N the Avogadro number, a the radius of the particles of the diffusing substance, and η is the viscosity of the medium.

By a method in which observations are made on small quantities of solution contained in short tubes of capillary diameter, necessitating the use of a micro-balance for the determination of the extent to which the dissolved substance has diffused into the surrounding solvent after a measured time interval, the author has investigated the variation of the diffusion constant with the temperature by experiments on solutions of mannitol. The data obtained for temperatures ranging from 0° to 70·2° show that the observed rate of diffusion is in satisfactory agreement with Einstein's formula. The average value of the radius of the mannitol molecule, calculated from this formula, is $3·9 \times 10^{-8}$ cm. H. M. D.

Studies in Dialysis. I. Dialysis of a Colloidal Solution of Hydrated Chromic Oxide in Chromic Chloride. MARKS NEIDLE and JACOB BARAB (*J. Amer. Chem. Soc.*, 1916, **38**, 1961—1970). —A number of experiments are described on the diffusion of solution of hydrated chromic oxide in chromic chloride solution. The experiments were carried out in three ways: (1) continuous dialysis, in which the diffusate was kept at constant level, but not changed during the process; (2) intermittent dialysis, in which the diffusate was continuously changed at the rate of 800 c.c. per hour. It is shown that in intermittent or continuous dialysis in a parchment membrane, colloidal particles diffuse through the membrane. In intermittent dialysis, the ratio $\frac{1}{3}$Cr : Cl in the diffusate after a short time is always greater than unity. In general, it is greater the longer the interval of dialysis for the same diffusate. In continuous dialysis, the ratio of $\frac{1}{3}$Cr : Cl in the diffusate increases from unity to a maximum of 1·57, then gradually diminishes and approaches zero. In intermittent dialysis, about 6% of the original colloid, still associated with considerable electrolyte, remains in the membrane at the end of fifty-six days and the colloid still diffuses, so that by continuing the process the whole of the colloid could be removed from the membrane. In the continuous dialysis, 75% of the original colloid remains in the membrane. Continuing the process for thirty-five days increases the purity of the colloid without loss of chromium. If the intervals in intermittent dialysis are made smaller, more satisfactory results are to be expected. In fact, by conducting the entire process in very short intervals, the efficiency may even exceed that of continuous dialysis. The latter procedure is, however, impractical. The variations in the ratio of $\frac{1}{3}$Cr : Cl in the diffusates are accounted for on the assumption of a gradual growth of the particles. In the intermittent process, the particles do not grow sufficiently to be retained by the membrane, whereas in the continuous process they do. The growth of the particles is explained partly by Bredig's theory of colloidal precipitation and partly by the assumption that the nuclei of the particles grow as the adsorbed chromic chloride is hydrolysed by the adsorbed water. J. F. S.

Osmotic Pressure of Sucrose Solutions at 30°. J. C. W. FRAZER and R. T. MYRICK (*J. Amer. Chem. Soc.*, 1916, **38**, 1907—1922).—The osmotic pressure of solutions of sucrose has been measured at 30° for concentrations up to that of a saturated solution. The apparatus employed is a modified form of that previously used by Morse and Frazer. The apparatus consists of a porous clay cell which carries the semi-permeable membrane on the outside. This cell is supported by its neck inside a bronze cylinder, to which the manometer is attached. The solvent is placed inside the porous cell and the solution in the bronze cylinder outside the porous cell. In this way a stronger membrane is produced and a greater area of active surface. The manometer used consists of a coil of Therlo wire which is immersed in oil. This metal changes its resistance in a perfectly regular manner with

pressure, so that by measuring the change of resistance of the coil the osmotic pressure of the solution with which it is in contact is at once known. This apparatus is much more rapid in its action than the older one, measurements being generally completed in ten to twenty-four hours. The water was tested at the end of each experiment for sugar which might possibly have passed through the membrane. It is shown that for solutions up to $5M$ no sugar passed through, and even for the strongest solutions examined the amount which passed through would only produce an error of 0·1 atm. in the osmotic pressure measurements. Pressures were obtained up to 270 atms. The results of the experiments are compared critically with those of other experimenters. In a theoretical discussion of the results, the Morse and Frazer modification of the van't Hoff equation is compared with van Laar's thermodynamic equation, using the mol. fraction basis. The authors recognise the necessity of using this basis in calculating the osmotic pressure of concentrated solutions. The experimental values obtained are compared with the theoretical values calculated by means of van Laar's equation, assuming various degrees of hydration of the dissolved sugar. It is pointed out that, although the theoretical calculations are based on assumptions and neglect certain factors, the evidence indicates that the hydrates of sucrose formed in aqueous solution are not of constant composition, as has been assumed, but are of variable composition. The degree of hydration decreases with increase in the concentration of the sugar.

J. F. S.

The Crystalline Liquids obtained by Evaporation of a Solution. PAUL GAUBERT (*Compt. rend.*, 1916, **163**, 392—394).—A description of the liquid crystals obtained by deposition from solutions of the following substances: anisylidene-*p*-aminoazotoluene, ethyl anisylideneaminocinnamate, *p*-azoxyanisole, cholesteryl esters, and active amyl cyanobenzylideneaminocinnamate. This method of production of liquid crystals permits of the measurement of their indices at the ordinary temperature. W. G.

Theory of Colloids. JOHN ARTHUR WILSON (*J. Amer. Chem. Soc.*, 1916, **38**, 1982—1985).—Further reasoning in favour of the author's theory of colloid formation (T., 1915, **109**, 307) (compare Beans and Eastlack, this vol., ii, 89). The main point in the theory is that the colloidal state in sols owes its stability to the formation of a complex between the particles of the disperse phase and certain substances present or formed in the dispersion medium during the preparation of the colloid. The main point in the present paper is an application of Donnan's work on membrane equilibria (A., 1911, ii, 848; T., 1911, **101**, 1554) to the distribution of ions in the layer of solution surrounding the colloidal particle, and the relation of this to the distribution in the bulk of the dispersion medium. It is deduced from this that $z = \sqrt{4ex + e^2}$, in which z is the concentration of ions bound to the colloid by electrochemical attraction, x the concentration of negative or positive ions in the

bulk of the solution, y the concentration of ions of the same charge as the colloid in the layer of solution surrounding the colloidal particle, and e the excess of concentration of diffusible ions of the surface layer over that in the bulk of the solution. The similarity of this expression with the usually accepted adsorption formula, $z = kx^{1/p}$, is noted, and as the value of $p = 2$, this becomes $z = k\sqrt{x}$. These two equations would, within limits, give similar adsorption curves. J. F. S.

Halogen Oxygen Compounds. XII. Kinetics of the Formation of Iodate from Iodine in Presence of the Tri-iodide Ion. ANTON SKRABAL and JOSEF GRUBER (*Monatsh.*, 1916, **37**, 535—548. Compare A., 1912, ii, 33; this vol., ii, 477).—The possibility of calculating the equilibrium constant $k_0 = [I_2][I'] / [I_3']$ from kinetic data relative to the formation of iodate has been referred to in a previous paper, and the method by which this result may be attained is now described. The two velocity equations concerned are respectively $d[IO_3']/d\theta = K_c[I_3']^3 . [OH']^4/[I']^6$ and $d[IO_3']/d\theta = K_c'[I_2]^3 . [OH']^4/[I']^3$, the coefficients in which are related to k_0 by the equation $K_c/K_c' = k_0^3$.

The data required to test this relation were obtained from experiments on the rate of formation of iodate, in which the conditions were adjusted so that the iodide and iodine concentrations, as determined by analysis, and the [OH'] concentration remained constant. Constancy of [OH'] was attained by the use of regulator mixtures consisting of $Na_2HPO_4 + NaH_2PO_4$. The results are in agreement with the above theoretical deduction.

It is further shown that the heat of formation of tri-iodide from iodine and the iodide may be derived from the temperature-coefficients of the rates of formation of iodate, and the result is in approximate agreement with that given by calorimetric measurements. H. M. D.

Isothermal Equilibrium of the System Crystallised Calcium Carbonate and Aqueous Ammonium Chloride. T. WARYNSKI and S. KOUROPATWINSKA (*J. Chim. phys.*, 1916, **14**, 328—335).—The solubility of calcite and aragonite in solutions of ammonium chloride of various concentrations from $0{\cdot}02N$ to N has been determined at 60°. In all cases, aragonite is more soluble than calcite, the ratio of the solubilities being about 1·17. Comparative experiments with sodium chloride and potassium chloride show that the solubility in ammonium chloride is about twenty times that in solutions of the above-mentioned salts. The increased solubility in ammonium chloride is held to be due to the formation of free, undissociated carbonic acid formed from the hydrogen ions produced in the hydrolysis of the ammonium chloride. The equilibrium set up when crystallised calcium carbonate is placed in an aqueous solution of ammonium chloride is in accordance with the equation $C_{Ca^{\cdot\cdot}} \times C_{H_2CO_3}/C_{[NH_4Cl]} = \pi K_k/K_c$ = constant, in which π is the solubility product of calcium carbonate, K_h is the hydrolysis constant of ammonium chloride, K_c is the dissociation constant of carbonic

acid, and $K_{[NH_4Cl]}$ is the concentration of the dissociated ammonium chloride. J. F. S.

The System Iron–Carbon–Oxygen. W. REINDERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 175—188).—A discussion of the conditions determining the equilibria in which mixtures of carbon monoxide and carbon dioxide form the gas phase, and iron, carbon, the oxides of iron, and iron carbide represent the solid phases. The data obtained by previous observers afford the material on which the analysis of the system is based. H. M. D.

Reaction Velocity–Temperature Studies. I. The Magnitude of the Temperature Coefficient of Reaction Velocity. ANTON SKRABAL (*Monatsh.*, 1916, **37**, 495—534).—Experimental observations relating to the influence of temperature on the velocity of chemical change have led to the formulation of certain empirical rules, according to which the ratio of the velocities for a given difference of temperature is approximately the same for all reactions. For an interval of 10°, the quotient $Q_{10°} = k_{t+10°}/k_t$ has a value which in most cases lies between 2 and 3, although recent work indicates that the limiting values of $Q_{10°}$ are more widely separated.

The reaction velocity–temperature rule takes no account of the variation of $Q_{10°}$ with the temperature, although there is abundant evidence to show that this quantity diminishes with rise of temperature. In other words, $Q_{10°}$ is a function of the temperature, and the formulation of the connexion between the temperature coefficient and the temperature obviously involves the more fundamental question of the dependence of the reaction velocity on the temperature.

This question is discussed in some detail, and by a special line of argument which avoids the usual conception of dynamic equilibria it is shown that the connexion between the velocity coefficient k and the temperature T may be expressed by the equation $\log_e k = -A/T + B \log_e T + CT + \phi(T) + J$, in which A, B, C, and J are constants. The various approximation formulæ which have been put forward from time to time to express the results of experiment are shown to be deducible as special cases from this general equation. The formula $\log_e k = -5249/T + 15{\cdot}865 \log_e T - 40{\cdot}16$ suggested by Bodenstein to express the results of his observations on the rate of decomposition of hydrogen iodide is specially considered, and by extrapolation it is shown that this at high temperatures leads to values of $Q_{10°}$ which approximate to unity, and at low temperatures to very high values of $Q_{10°}$, which, moreover, increase very rapidly as the temperature falls. If extrapolation of such an equation is permissible, the conclusion to be drawn from the results is that the temperature coefficient diminishes, and approximates to unity when the velocity becomes very great and increases rapidly when the velocity becomes very small. Reactions of measurable velocity fall for the most part within limits which correspond with a normal value of the tempera-

ture coefficient. There are, however, certain reactions which are anomalous in this respect. An example is afforded by the spontaneous decomposition of enzymes, the temperature coefficient of which is abnormally large.

The relation between the reaction velocity and other variables which affect the velocity is said to be of the same kind as that between the reaction velocity and the temperature. Such variables are the nature and constitution of the reacting substances, the nature of the reactive medium, catalytic agencies, and the action of light. In other words, the changes in the reaction velocity which are produced by alterations in any of these variables may be expressed by a general parameter rule, according to which the change in the reaction velocity resulting from a change in any one of the independent parameters diminishes as the order of magnitude of the reaction velocity increases. Experimental results which afford support for the validity of the rule are examined.

H. M. D.

Influence of Strong Salt Solutions on the Spontaneous Oxidation of Pyrogallol, Ferrous Sulphate, and Lævulose. C. G. MacArthur (*J. Physical Chem.*, 1916, **20**, 545—553).—The influence of solutions of sodium chloride, magnesium chloride, potassium nitrate, sodium bromide, potassium chloride, and sodium sulphate on the rate of oxidation of pyrogallol, ferrous sulphate and lævulose by air at 20° has been ascertained. The solutions of salts used were of concentrations varying from N to $8N$, and these were made up in $N/10$-sodium hydroxide. The experiments were carried out by placing 50 c.c. of the given salt solution and a weighed amount of the oxidisable substance in a 400 c.c. flask fitted with a thermometer and a manometer. The progress of the reaction was ascertained by the change in the pressure. It is shown that all the salts examined decrease the rate of oxidation, and this is due to the decreased solubility of the oxygen in the solution. Sodium chloride, potassium chloride, and potassium nitrate have about the same effect on the rate of oxidation; sodium bromide decreases the solubility of oxygen more than the abovementioned salts, and in consequence decreases the rate of oxidation more. Sodium sulphate and magnesium chloride are more marked in their action than sodium bromide. In all experiments with increase in the salt concentration there is a decrease in the rate of oxidation. The curves representing the rate of oxidation run parallel with those representing the solubility of oxygen in all cases except those of lævulose in dilute salt solutions. J. F. S.

The Velocity of Hydration of the Anhydrides of some Fatty Acids. III. P. E. Verkade (*Rec. trav. chim.*, 1916, **36**, 194—213. Compare A., 1914, ii, 256; this vol., ii, 234, 374).—The velocities of hydration of the anhydrides of β-methylbutyric, α-methylbutyric, and α-ethylbutyric acids have been measured at 25° by the conductivity method and the coefficients ($0·4343k$) calculated, assuming the actions to be unimolecular. In every

case it was found that the coefficient steadily diminished with the time, thus showing that the action is not unimolecular, but a much more complicated process. W. G.

The Rates of Solution of Metals in Ferric Salts and in Chromic Acid. R. G. VAN NAME and D. U. HILL (*Amer. J. Sci.*, 1916, [iv], **42**, 301—332).—In previous papers (A., 1910, ii, 280; 1911, ii, 973) it has been shown that eight different metals dissolve in solutions of iodine in potassium iodide at the same (equivalent) rate. The observations indicate that the rate of dissolution is determined essentially by the rate at which iodine diffuses to the surface of the metal. Similar experiments have now been made with solutions of (*a*) ferric sulphate and sulphuric acid; (*b*) ferric chloride and hydrochloric acid; (*c*) chromic acid and sulphuric acid. In each series of experiments the influence of varying concentration of the acid was examined.

The results obtained show, as before, that the rate of dissolution in the more strongly acid solutions has the same value for different metals when the conditions are the same. The determining factor is the rate of diffusion of the oxidising agent to the surface of the metal. With increasing concentration of sulphuric acid, the rate of dissolution of the metals decreases, and in terms of the diffusion theory this may be readily explained by the increased viscosity of the solution. In the more dilute acid solutions, the observed rates depend to some extent on the nature of the metal, the sequence of the metals corresponding approximately with that of the metals in the electromotive series, and the rate of dissolution increasing with the electropositive character of the metal. For both dilute and stronger acid solutions, the rate is proportional to the concentration of the oxidising agent.

The observations lead to the conclusion that the rate of dissolution in the more strongly acid solution is determined almost entirely by the velocity of diffusion of the oxidising agent; in the less strongly acid solutions, on the other hand, where the rates of dissolution vary somewhat according to the nature of the metal, it seems that the velocity of the chemical process at the surface of the metal has a measurable influence on the observed rate of dissolution.

Whether the measured rate of dissolution is determined solely by the diffusion process or not, it can be shown that the equation for a unimolecular reaction is applicable. In other words, the course of the dissolution process is independent of the relative rate of the diffusion process and the chemical reaction at the surface of solid and solution.

The behaviour of silver is anomalous, for although in ferric sulphate solutions increasing acidity tends to bring it into line with the other metals, as might be expected, according to the above views the effect of increasing acidity in chromic acid solutions is to increase the difference between the rate of dissolution of silver and of the metals which behave normally. Whether silver is an exception to the general behaviour, or whether the observed results

are to be ascribed to some unknown disturbing factor, cannot be determined from the evidence at present available. H. M. D.

Catalytic Hydrogenation of Organic Compounds with Base Metals at the Ordinary Temperature. II. Influence of Contact Poisons on the Hydrogenation. C. KELBER (*Ber.*, 1916, **49**, 1868—1879. Compare this vol., ii, 309).—The influence of potassium cyanide, hydrogen cyanide, hydrogen sulphide, and carbon disulphide on hydrogenations in the presence of the three catalysts: I, nickel prepared by heating basic nickel carbonate at 450° in a current of hydrogen; II, the same prepared at 310°; and III, nickel on an inorganic support, prepared by heating the carbonate, spread over the support, at 450° in hydrogen, has been quantitatively studied, the reduction of an alkaline solution of sodium cinnamate again serving for the test reaction.

The catalyst I is easily "poisoned"; II requires larger quantities of the anti-catalysts to stop its action; whilst III is resistant to the "poisons." Potassium cyanide is the most active poison, the amounts required to prevent the exertion of the influence of 0·5 gram of the catalyst being: I, 0·0003 gram; II, 0·001 gram; III, 0·02 gram respectively. Hydrogen cyanide is not so active, owing to its rapid alteration by the hydrogen under the influence of the nickel; (in this case, solutions quite free from alkali were used, which precluded tests with catalyst III). The poisoned catalyst is still inactive after washing it free from these cyanides. It can be gradually regenerated if it is shaken with hydrogen during the washings or by washing it with ammonia solution, which does not remove detectable amounts of nickel, showing that nickelous cyanide is not formed. It is most readily regenerated, however, by boiling with sodium hydroxide, whereby ammonia is evolved.

Hydrogen sulphide acts as a poison by forming chiefly nickel sulphide, the "fatal doses" for 0·5 gram of the catalysts being 0·005, 0·02, and 0·1 gram respectively. Carbon disulphide also gives nickel sulphide, and the limiting quantities in the three cases are: 0·003, 0·01, and more than 0·06 gram. J. C. W.

Catalytic Decomposition of Hydrogen Peroxide in Certain Non-aqueous Solutions. JAMES H. WALTON and DEWITT O. JONES (*J. Amer. Chem. Soc.*, 1916, **38**, 1956—1961).—The action of a number of salts of cobalt, copper, lead, manganese, nickel, silver, iron, mercury, ammonium, cadmium, lithium, calcium, potassium, sodium, and strontium on solutions of hydrogen peroxide in amyl acetate, amyl alcohol, *iso*butyl alcohol, and quinoline has been studied. It is shown that most of these substances act in just the same way toward the hydrogen peroxide as they do in water solution. The velocity of decomposition of hydrogen peroxide in quinoline solution by manganese acetate was studied. In this connexion it is shown that if not more than 2% of water is present the reaction is bimolecular, but if the quinoline is saturated with water, the reaction is unimolecular. Hydrogen peroxide is decomposed quantitatively by manganese acetate in quinoline solution.

If the catalyst is present in so small a quantity that the reaction is slow, a side reaction, namely, the oxidation of the quinoline by the hydrogen peroxide, is appreciably catalysed by the manganese acetate. In solutions containing the catalyst in high concentrations the velocity of the reaction is approximately doubled by doubling the concentration of the catalyst. It is shown that there is no simple relationship between the electrical conductivity of solutions of manganese acetate in quinoline saturated with water and the velocity with which the peroxide is decomposed in such solutions. J. F. S.

Atomic Structure. L. Zehnder (*Ber. Deut. physikal. Ges.*, 1916, **18**, 324—332).—A theoretical paper in which the structure of atoms is considered from the hypothesis that they are built up of a perfectly elastic nucleus which is pressed together by an enormous æther pressure. The author imagines the atoms built up of hydrogen atoms; in the first place four hydrogen atoms, assumed to be spherical, are arranged to form a tetrahedron, which on account of its great stability represents the formation of the helium atom. The carbon atom is then regarded as built up from three such helium atoms. From the form of the carbon atom so constructed the author evolves structures for the paraffins and olefines. A formula is evolved for the benzene ring and the naphthalene double ring, which portray the stability of these substances. In the case of benzene it is interesting to note that according to this method of representation it should exist in two optically active forms. Formulæ are also devised for the sugars, sucrose, and dextrose on the same plan. From three helium nuclei and two hydrogen atoms an atom is constructed which from its form should be somewhat inactive and should be both ter and quinque-valent. This the author regards as the structure of nitrogen. In somewhat the same way the atom built up from four helium nuclei (oxygen) is shown to be chemically very active, whereas water produced from it is less chemically active. Two forms of hydrogen peroxide are constructed from the water model, the one perfectly symmetrical and the other unsymmetrical. J. F. S.

The Fundamental Values of the Quantities b and $\sqrt{a}$ for Different Elements in Connexion with the Periodic System. II. Mercury and Antimony. General Methods. J. J. van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 2—24).—In a previous paper (this vol., ii, 386) it has been shown that the values of b and $\sqrt{a}$ for substances in the critical condition are additive in nature and can be calculated from constants characteristic of the elements which are present in the compounds. The present paper is mainly concerned with a discussion of methods for obtaining a and b without a knowledge of the critical data, p_c and T_c.

By reference to mercury and antimony it is shown that the value of b for metallic elements may be derived from the density of the solid halogen compounds. If the equation corresponding with the

law of rectilinear diameters is written in the form $\frac{1}{2}(d_1+d_2)=1+\gamma(1-m)$, and if at the reduced temperature, m, the density, d_2, of the saturated vapour is negligible in comparison with the density d_1 of the co-existing liquid, then it may be shown that $b=v_1\times 2\gamma[1-\gamma m/1+\gamma]$, in which v_1 is the molecular volume of the liquid at the reduced temperature expressed in terms of the normal gas volume. Since the density of the liquid differs but little from that of the substance in the solid state, the value of v_1 is given approximately by the density of the solid. Having obtained in this manner the values of b for the halogen compounds, the value of b for the metallic element may be derived on the basis of the additivity of b.

Assuming that the critical temperatures or pressures of the halogen compounds are known, the values of a may be calculated from the equation $T_c=78{\cdot}03a/b$ or $p_c=a/28b^2$, and the additivity of $\sqrt{a}$ made use of in the deduction of a for the metallic element with which the halogens are combined.

When the critical pressure p_c is not known, it may be got from vapour pressure data by making use of the relation $(\log p_c-\log p_1)/(\log p_c-\log p_2)=T_2(T_c-T_1)/T_1(T_c-T_2)$, in which p_2 and p_1 are the vapour pressures of the liquid substance at temperatures T_2 and T_1 respectively.

When T_c is unknown, it may be obtained from the empirical relation $T_c/T_s=1{\cdot}60$, in which T_s is the boiling point of the liquid at atmospheric pressure.

Attention is drawn to the circumstance that the tabulated values of b and $\sqrt{a}$ for the various elements cannot be applied to the elements themselves unless the molecular condition of the elements in the critical state is taken into account. A knowledge of this is necessary before the values of p_c and T_c for the elements can be calculated from the atomic values of $\sqrt{a}$ and b.

The fact that the critical temperatures of certain elements are very much higher than those calculated from the equation $T_c=78{\cdot}03a/b$ is considered to show that these elements in the critical condition consist of molecules which contain several and in some cases a great many atoms. Mercury in the critical state thus appears to consist of diatomic molecules, whilst the molecules of antimony contain about 12 atoms and molecules of carbon about 80 atoms.

In the former paper it was pointed out that ter- and quadrivalent atoms have no influence on the value of the attraction constant a of these symmetrical compounds. The absence of this effect in compounds such as methane, carbon tetrachloride, stannic chloride, and ammonia is to some extent responsible for the low critical temperature of these substances and their relatively great volatility. H. M. D.

The Functions of the Higher Valencies. ARTHUR CLAYTON (T., 1916, **109**, 1046—1050).—The successive groups of the periodic table show a continuous increase in the oxygen valency, whilst the hydrogen valency rises to a maximum and then falls regularly.

The phenomenon is supposed to be due to a difference in the actual nature of the hydrogen and oxygen valencies. This difference is brought to light by a comparison of the actual types of hydrogen and hydroxyl compounds which are characteristic of the periodic groups. These types show that the maximum number of hydrogen atoms increases from one to four in the first four groups and then remains constant throughout the subsequent groups. The four valencies involved in the attachment of these hydrogen atoms may also bind hydroxyl groups, and these are termed "primary" valencies. In the fifth group a new type of valency appears which is incapable of binding hydrogen atoms, although it suffices for the attachment of hydroxyl groups. This "secondary" valency increases regularly from the fifth to the eighth group. The elements of the fifth, sixth, seventh, and eighth groups have therefore four primary valencies and one, two, three, and four secondary valencies respectively.

As a result of the tendency for primary and secondary valencies to unite, the apparent valency of an element may be less than the maximum valency by two, four, six, or eight units. This view may be advantageously applied in representing the valency relations of unsaturated compounds. H. M. D.

Industry and Education. H. REISENEGGER (*Ber.*, 1916, **49**, 1535—1539).—An address delivered to the German Chemical Society in Berlin. J. C. W.

Inorganic Chemistry.

Preparation of Hydrogen Peroxide. F. COBELLIS (U.S. Pat., 1195560; from *J. Soc. Chem. Ind.*, 1916, **35**, 1059).—Hydrogen peroxide is produced by the decomposition by heat of ammonium persulphate in a solution containing the latter and ammonium hydrogen sulphate. The process is applied continuously by electrolysing a solution of ammonium sulphate at a comparatively low temperature so as to form ammonium persulphate, heating the solution under pressure so as to form ammonium sulphate and hydrogen peroxide, and finally distilling off the latter under reduced pressure in a current of an inert gas. The residual solution of ammonium sulphate can then be put through the same cycle of operations again. H. W.

Chemical Action of Sodium Peroxide on Hydrogen Sulphide. C. ZENGHELIS and STAVROS HORSCH (*Compt. rend.*, 1916, **163**, 440—442).—When hydrogen sulphide is passed over sodium peroxide, a very vigorous action occurs either in the presence or the absence of air, and if the peroxide is previously warmed, the action is accompanied by a flame and the containing vessel of

glass or porcelain is attacked. The products of the action vary according to the conditions. The hydrogen of the hydrogen sulphide always goes to form water, which in its turn partly attacks the hydrogen peroxide. In the absence of air the sulphur forms sodium sulphide and polysulphides, together with a small amount of thiosulphate and sulphate, and if the current of hydrogen sulphide is rapid there is a deposition of a small amount of free sulphur. In the presence of air scarcely any sulphide is formed, but sodium sulphate and free sulphur are obtained. If the containing vessel is attacked owing to a very vigorous action, then the solid products have a blue tinge, due to the iron in the glass or porcelain. W. G.

Preparation of Hypochlorous Acid. W. N. HAWORTH and J. C. IRVINE (Eng. Pat., 12912; from *J. Soc. Chem. Ind.*, 1916, **35**, 1059).—Chlorine, derived from the liquid element, is bubbled through a series of bottles which are agitated on a shaking machine and contain water, together with a catalyst, which is preferably a salt or oxide of copper, but may also be a nickel or cobalt salt. The resulting liquid, which contains about 2% of hypochlorous acid, may be freed from dissolved copper by precipitation or by distilling off the acid. For each bottle of $1\frac{3}{4}$ litres capacity from 80 to 100 grams of catalyst are used, but in the case of copper oxychloride only 10 grams are necessary. H. W.

The Iodine Content of Stassfurt Sylvine and Carnallite. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1916, **29**, i, 342—343).—Sylvine and carnallite were tested for traces of iodine by treatment with nitrous acid and carbon tetrachloride, whereby 0·05 mg. could be detected in 10 grams of salt. In the event of a negative result, the colourless carbon tetrachloride extracts were treated with 1 c.c. of water and two drops of 0·1% sulphurous acid in a small separating funnel, and the aqueous extract was again treated with nitrous acid and 1 c.c. of carbon tetrachloride, when 0·005 mg. of iodine produced a visible coloration. The quantitative estimation was carried out either colorimetrically or by titration with thiosulphate, according to the quantity present. In the latter case, the iodine was oxidised by chlorine water, the chlorine and bromine boiled off, and the iodate then decomposed by the addition of phosphoric acid and potassium iodide. The results indicated that certain specimens of both sylvine and carnallite were free from iodine, whilst others contained quantities varying from 13 to 73 mg. per kilo. of sylvine and 1 to 5 mg. per kilo. of carnallite. In no case could iodate be detected, and the iodine must therefore have been present as iodide. Crude bromine was found to be free from iodine. G. F. M.

The So-called Alkali Ozonates. WILHELM TRAUBE (*Ber.*, 1916, **49**, 1670—1679. Compare A., 1912, ii, 844).—The behaviour of "potassium ozonate" on keeping and on treatment with water or dilute acids is discussed. It is known to lose its colour in time

and to change into potassium hydroxide, oxygen, and potassium tetroxide. Since the latter yields ordinary oxygen and hydrogen peroxide on treatment with water, it may be written as a compound of a higher order (according to Werner), thus, $K\cdot O\cdot O\cdot K,O_2$, and the reactions of the ozonate, which may also be written as $(KOH)_2,O_2$, may then be expressed as follows: $3[(KOH)_2,O_2] = 2K_2O_2,O_2 + 2KOH + 2H_2O$, $2[(KOH)_2,O_2] = 2K_2O_2 + 2H_2O + O_2$, and $K_2O_2 + (KOH)_2,O_2 = K_2O_2,O_2 + 2KOH$.

It is supposed that ozone breaks down into oxygen and atomic oxygen in contact with the alkali, and that it is only the latter which reacts. This would account for the fact that no more powerful oxidising agent is obtained.

Rubidium and cæsium hydroxide form orange-red ozonates, and cæsium carbonate also becomes temporarily orange-coloured in a current of ozone.

The author therefore recognises four classes of metallic oxides: the ordinary basic oxides, oxides like manganese dioxide, oxides which yield hydrogen peroxide, and oxides of a higher order, like potassium tetroxide. J. C. W.

The Nature of Subsidiary Valencies. XIII. Complexes with Sulphur Dioxide. FRITZ EPHRAIM and ISAAC KORNBLUM (*Ber.*, 1916, **49**, 2007—2021. Compare this vol., ii, 104; 1915, ii, 441, etc.).—Although many salts with complex anions are known, few of them lend themselves to studies of their thermochemical dissociation. A series of complexes has now been obtained by combining various salts (iodides and thiocyanates chiefly) with sulphur dioxide in the cold, and the heats of formation and dissociation temperatures have been determined. The stability of the alkali iodide complexes with $4SO_2$ rises with increasing atomic weight of the metallic atom, but the reverse is the case with the alkaline earth iodides and all the thiocyanates. According to the authors' views, the influence of the central metallic atom should always be exerted in one way if the anion is complex, and in the opposite if the cation is complex, and the above discrepancies are explained, on plausible grounds, by assuming that the sulphur dioxide can enter into both ions. The iodides also occur in two series, yellow and red, and this points to the existence of such isomerides as, for example,

$$\left[M(SO_2)_4\right]\left[M{}^{I_2}_{(SO_2)_4}\right] \text{ and } \left[M(SO_2)_6\right]\left[M{}^{I_2}_{(SO_2)_2}\right].$$

Lithium iodide forms two dichromate-coloured *compounds*, LiI,SO_2 and $LiI,2SO_2$, the former at 0°, the latter at lower temperatures. Sodium iodide forms the red *compound*, $NaI,2SO_2$, at 0°, and the pale yellow *compound*, $NaI,4SO_2$, in a freezing mixture. Potassium iodide yields the red compound, $KI,4SO_2$ (Walden, A., 1903, ii, 284). The *compound* $RbI,4SO_2$, m. p. 13·5°, is lemon-yellow; the *compound* $CsI,4SO_2$ is canary-yellow. Barium iodide forms the orange-red *compound*, $BaI_2,4SO_2$, and the yellowish-red *compound*, $BaI_2,2SO_2$; the *compounds* $SrI_2,2SO_2$ and

$SrI_2,4SO_2$ are red; the red *compound*, $CaI_2,4SO_2$, tends to decompose with the liberation of iodine.

Potassium thiocyanate forms lemon-yellow *compounds* with 0·5 and $1SO_2$, rubidium, cæsium, and calcium thiocyanates form yellow compounds with $0·5SO_2$ per molecule.

The aluminium haloids apparently combine with $1SO_2$ at low temperatures.

The above compounds are tabulated with their dissociation temperatures and heats of formation. J. C. W.

Behaviour of Tellurium towards Hydrogen Peroxide. GEORG SCHLUCK (*Monatsh.*, 1916, **37**, 489—494).—The behaviour of tellurium towards hydrogen peroxide is found to depend on the physical condition of the element. Colloidal tellurium is acted on by very dilute solutions of the peroxide, whilst the crystalline modification only reacts slowly with 60% hydrogen peroxide at 100°. The rate of dissolution increases with the amount of telluric acid formed. Amorphous tellurium, precipitated from hydrochloric acid solution by sulphur dioxide and dried at 105°, behaves similarly to crystalline tellurium, but if the amorphous variety is dried by treatment with alcohol and ether, it dissolves quite readily in concentrated hydrogen peroxide solutions. H. M. D.

Active Nitrogen. Postscript. ERICH TIEDE (*Ber.*, 1916, **49**, 1741—1742).—The attention of German chemists is directed to the recent work of Strutt (A., 1915, ii, 336), which was the outcome of the collaboration of Baker, Domcke, Strutt, and Tiede in July, 1914. J. C. W.

Catalysis of Azoimide. I. E. OLIVERI-MANDALA (*Gazzetta*, 1916, **46**, ii, 137—159).—The author has investigated the action exerted on aqueous solutions of azoimide by finely subdivided platinum in the form of a colloidal solution of the metal, platinum-black, and spongy platinum.

The gas liberated during the catalysis of azoimide by platinum-black consists solely of nitrogen, and estimations of the amounts of this gas and of ammonia formed from a certain quantity of the azoimide show that the reaction may be expressed by the equation $3N_3H = 4N_2 + NH_3$. This final result is probably obtained by way of the intermediate stages $3N_3H = 3NH + 3N_2$, $3NH = (NH)_3$, and $(NH)_3 = NH_3 + N_2$. If the catalysis occurs under ordinary conditions, the constant for a unimolecular reaction diminishes very considerably as the reaction proceeds, but if the liquid is stirred to render it uniform and to facilitate the liberation of the gas formed in the solution, the value of the constant undergoes only very slight alteration.

Hydrogen occluded in platinum foil decomposes azoimide three times as rapidly as does oxygen similarly occluded.

Colloidal platinum exhibits only feeble activity in the decomposition of azoimide in aqueous solution, and this result is shown to be due to a "poisoning" of the platinum by the azoimide; the

alkali salts of the latter exert a similar poisoning action on colloidal platinum. T. H. P.

Chemical Action of Sodium Peroxide on the Oxides of Carbon. C. ZENGHELIS and STAVROS HORSCH (*Compt. rend.*, 1916, **163**, 388—390. Compare Harcourt, this Journal, 1861, **14**, 267; 1862, **15**, 381).—Carbon monoxide reacts rapidly with sodium peroxide, the temperature rising slightly, and sodium carbonate being formed. Carbon dioxide reacts with a much greater intensity, the temperature rising considerably, free, active oxygen being liberated. The thermal effect, according to the equations, being greater in the first case than in the second, the difference in the violence of the reactions is explained on the grounds that in the second case the endothermic compound, sodium percarbonate, is formed as an intermediate product, and decomposes immediately it is formed, the temperature thus rising and the reaction proceeding more rapidly.

If carbon dioxide is passed over mixtures of sodium peroxide with such oxidisable substances as aluminium, magnesium, wood, etc., the reactions proceed with extreme violence, often giving rise to explosions. W. G.

The Decomposition of Alkali and Alkaline-Earth Azides in a High Vacuum for the Preparation of Pure Nitrogen. ERICH TIEDE (*Ber.*, 1916, **49**, 1742—1745).—The following table gives, I, the temperatures at which various azides begin to decompose in the vacuum of a Gaede pump; II, the temperatures at which the evolution of nitrogen is steady, which are regularly lower than the initial points in the case of the alkaline earths, owing, no doubt, to the catalytic influence of the finely divided metal; and III, the melting points:—

	Na.	K.	Rb.	Cs.	Ca.	Sr.	Ba.
I.	330°	320°	260°	290°	110°	140°	160°
II.	280	360	310	350	100	110	120
III.	—	350	300	320	—	—	—

J. C. W.

Manufacture of Products containing Sodium Pyrophosphate and Active Oxygen. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (Brit. Pat., 1915, 15749; from *J. Soc. Chem. Ind.*, 1916, **35**, 1015—1016).—If hydrogen peroxide (3 mols.) and sodium pyrophosphate (1 mol.) are caused to react, a solid, dry product containing active oxygen equivalent to more than 27% of hydrogen peroxide is obtained. H. W.

Preparation of Sodium Percarbonate. HENKEL & Co. (Brit. Pat., 1916, 100997; from *J. Soc. Chem. Ind.*, 1916, **35**, 963).—Sodium percarbonate, $2Na_2CO_3,3H_2O_2$, is obtained by treating at 0° sodium carbonate with an aqueous solution of hydrogen peroxide in the proportion of not less than 3 mols. of the latter to 2 mols. of the former; the product is dried in a vacuum. H. W.

Aqueous Solutions of Ammonium Carbonate; and Hydrolysis in General. RUD. WEGSCHEIDER (*Monatsh.*, 1916, **37**, 425—472).—The solubility of certain carbonates in solutions of ammonium carbonate may be due to the formation of complex metallo-carbonate anions or complex cations containing ammonia, or it may be due to the transformation of carbonate into hydrocarbonate ions or the solvent action of hydroxyl ions. Before it is possible to assign the solvent action of the ammonium carbonate to one or other of these causes, it is necessary to have more or less precise information relative to the constitution of ammonium carbonate solutions. These solutions may contain the following kinds of molecules (or ions): NH_3, $NH_4{\cdot}OH$, CO_2, H_2CO_3, HCO_3', CO_3'', OH', $H^{\cdot}$, together with undissociated molecules of water and salt. If ammonium carbonate is present, the presence of $NH_2{\cdot}CO_2H$, $OH{\cdot}NH_3{\cdot}CO_2H$, $NH_2{\cdot}CO_2'$, and $OH{\cdot}NH_3{\cdot}CO_2'$ must also be assumed.

An attempt is made to determine the concentration of the various molecular and ionic species, and in this way to afford a basis of the explanation of the solvent action referred to above.

Incidentally, it is shown that the degree of hydrolysis of salts of weak acids and bases is not independent of the dilution unless the ionisation constants of the acid and base are approximately equal. The greater the departure from equality, the greater the variation of the hydrogen- and hydroxyl-ion concentration with the concentration of the salt.

The available data permit the derivation of the constant characteristic of the equilibrium between carbonate and carbamate. It would seem that ammonium carbamate is almost completely hydrolysed. H. M. D.

Ammoniates of Silver Salts. II. G. BRUNI and G. LEVI (*Gazzetta*, 1916, **46**, ii, 235—246).—It was found earlier (this vol., ii, 482) that silver salts of organic acids absorb two molecules of ammonia for each atom of silver present. The investigation has now been extended to the silver salts of acids containing an amino- or amido-group in the molecule and also to those of the amides and imides of certain acids.

Silver aminosulphonate combines with $2NH_3$ at 10° or at −18°; the silver derivative of glycine, with NH_3 at 10° or $2NH_3$ at −18°; the silver salt of alanine, with NH_3 at 10° or $2NH_3$ at −18°; silver *o*-aminobenzoate, with NH_3 at 10° or $2NH_3$ at −18°; silver aspartate, with $3NH_3$ at 10° or $4NH_3$ at −18°; the silver salt of asparagine, with NH_3 at 10° or $2NH_3$ at −18°; the silver derivatives of benzamide and succinimide, with NH_3 at either 10° or −18°; the silver derivative of phthalimide, with $2NH_3$ at either 10° or −18°; the silver derivative of carbamide fixes no more than traces of dry ammonia gas either at 10° or at −18°.

The supposition that amino- or imino-groups may replace molecules of ammonia in complex compounds and thus cause an equivalent diminution in the number of ammonia molecules absorbed, is thus verified within certain limits and with certain conditions. A marked regularity is observed with the salts of the true amino-

acids, these at the ordinary temperature fixing a molecule of ammonia less than the corresponding non-aminated acids, whereas at lower temperatures they absorb 2 mols. of ammonia per atom of silver. The capacity of the amino-group to replace a molecule of ammonia in complexes is therefore limited, and it ceases when the avidity of absorption of the ammonia increases at low temperatures. The absorption gives rise in succession to compounds of the two types, $CH_2<\substack{NH_2 \\ CO_2}>Ag\ldots NH_3$ and

$$NH_2\cdot CH_2\cdot CO_2Ag<\substack{NH_3 \\ NH_3}.$$

Such addition of ammonia in stages does not occur with the salts of non-aminated acids.

No explanation is suggested for the anomalous results obtained with the silver derivatives of succinimide, phthalimide, and carbamide. T. H. P.

The System Lime–Ferric Oxide. R. B. SOSMAN and H. E. MERWIN (*J. Washington Acad. Sci.*, 1916, **6**, 532—537).—The system lime–ferric oxide has been examined by means of temperature–time curves and by the optical properties of the resulting products. It is shown that, contrary to the statements of Kohlmeyer (A., 1910, ii, 35), only two calcium ferrites exist, and not five, as described by this author. The present authors describe the compound $2CaO,Fe_2O_3$ as a well-crystallised, black substance, the crystals of which are yellowish-brown by transmitted light. The melted substance may be supercooled to 1385°, but it always shows traces of its dissociation products, CaO,Fe_2O_3 and CaO. It is a positive biaxial substance with a moderate optic axial angle. $\alpha=2\cdot200\pm0\cdot005$, $\beta=2\cdot220\pm0\cdot005$, and $\gamma=2\cdot290\pm0\cdot005$ for lithium light, whilst for sodium light $\alpha=2\cdot25$, whilst β and γ have a lower dispersion. The transition temperature at which CaO,Fe_2O_3 dissociates and is in equilibrium with liquid and with $2CaO,Fe_2O_3$ is 1216°. The compound CaO,FeO_3 is deep red in colour; it is negative uniaxial, and has the following refractive indices: $\omega=2\cdot465\pm0\cdot005$, $\epsilon=2\cdot345\pm0\cdot005$ for lithium light, whilst for sodium light the values are about $\omega=2\cdot58$ and $\epsilon=2\cdot43$. It is shown that a considerable amount of ferrous oxide is formed in mixtures containing up to 50 molecular per cent. of lime, but for higher percentages of lime the amount of ferrous oxide formed is small at temperatures up to 1500°. A composition-temperature diagram of the various equilibria is given in the paper. J. F. S.

The Corrosion of French, Bohemian, and German Glass Vessels. PAUL NICOLARDOT (*Compt. rend.*, 1916, **163**, 355—357).—The author has compared laboratory vessels made from French (three samples), Jena (one sample), Bohemian (Krasna and Kavalier), and Thuringian glass as regards their resistance to attack by reagents and resistance to sudden changes of temperature. The reagents employed were boiling water, cold water, hydrochloric acid (10%), ammonium hydroxide (50% NH_3), $N/10$-ammonium chloride, and $N/10$-sodium carbonate. The glasses were also heated

with water under pressure up to 140°. In every case the behaviour of the French glass was quite comparable with that of the best German and Bohemian glass. For the resistance to sudden changes of temperature, conical flasks were filled with paraffin-wax and heated in a stove, the temperature of which was gradually raised from 100° to 225°. At intervals of 25° test flasks were taken out and plunged into cold water. The breaking temperature in the case of the French glass was about the same as that of the Bohemian and Thuringian glass, but lower than that of the Jena glass. Complete analyses are given of the various glasses.

W. G.

Action of Sulphur on Barium Hydroxide in the Presence of Water. L. GUITTEAU (*Compt. rend.*, 1916, **163**, 390—391).—When a mixture of 2 parts of barium hydroxide, 1 part of sulphur, and 25 parts of water is boiled, a deep brown, almost black liquid is obtained, which on cooling becomes orange-red in colour. If this solution is evaporated rapidly until a continuous crust is formed on the surface, on cooling the liquid, voluminous, red prisms of barium tetrasulphide, BaS_4,H_2O, are obtained, mixed with sulphur and barium thiosulphate. The orange-red liquid from which these were obtained contains barium and sulphur in the proportion corresponding with a barium pentasulphide, which appears to exist in solution, but decomposes during the evaporation.

W. G.

Preparation and Phosphorescence of Pure Magnesium Sulphide. I. ERICH TIEDE (*Ber.*, 1916, **49**, 1745—1749).—Two methods for the preparation of crude magnesium sulphide have been examined. According to Mourlot (A., 1899, ii, 27), the pure substance may be obtained by reducing magnesium sulphate in a current of hydrogen and hydrogen sulphide, but this cannot be realised by the present author. A modification of Reichel's method (1875), whereby red-hot, granular magnesium is submitted to a stream of hydrogen and sulphur vapour, gives a crude product containing 30—50% of sulphur.

The free metal in the crude sulphide can be removed by distillation at 600—700° in the vacuum of a mercury pump or by adding bromobenzene to an ethereal suspension, the sulphide being quite unaffected. Pure magnesium sulphide obtained in this way is a reddish-white, amorphous powder. It phosphoresces with a dim, white light, and responds best to long-wave light; radium, Röntgen, or ultra-violet rays are without influence on it, but in the cathode rays it exhibits a brilliant red and blue fluorescence and a faint phosphorescence. J. C. W.

Lead Arsenates. The Factors Controlling the Reactions of Lead Nitrate and Lead Acetate with Disodium [Hydrogen] Arsenate. G. ENNIS SMITH (*J. Amer. Chem. Soc.*, 1916, **38**, 2014—2027).—It is shown that the products of reaction of lead nitrate or acetate with disodium hydrogen arsenate are mixtures

of lead hydrogen arsenate, $PbHAsO_4$, and lead hydroxyarsenate, $Pb_5(OH)(AsO_4)_3$. The products of the reaction at low temperatures at equilibrium consist mainly of lead hydrogen arsenate. When very dilute solutions (less than 0·001*M*) are used, the hydroxyarsenate predominates if the precipitates are filtered as soon as they are formed. The precipitate first formed is lead hydroxyarsenate, but this undergoes a secondary reaction and becomes lead hydrogen arsenate. The quantity of lead hydrogen arsenate at equilibrium increases with increase in concentration of the reacting substances, whereas that of the hydroxyarsenate increases with increase of temperature and with excess of disodium hydrogen arsenate. The influence of ammonium hydroxide, borax, sodium metasilicate, sodium nitrate, and sodium salts of fatty acids on lead hydrogen arsenate has been studied. In every case, lead hydroxyarsenate is produced when lead hydrogen arsenate is shaken with solutions of the above-mentioned salts. The point of equilibrium of the two reactions,

$$5PbHAsO_4 + 4NaNO_3 + H_2O \rightleftharpoons Pb_5(OH)(AsO_4)_3 + 2Na_2HAsO_4 + 4HNO_3,$$

$$5PbHAsO_4 + 4CH_3{\cdot}CO_2Na + H_2O \rightleftharpoons Pb_5(OH)(AsO_4)_3 + 2Na_2HAsO_4 + 4CH_3{\cdot}CO_2H,$$

has been determined, and it is shown that from a knowledge of the point of equilibrium, the composition of the resulting lead arsenate may be calculated. J. F. S.

Lead Arsenates. I. C. C. McDonnell and C. M. Smith (*J. Amer. Chem. Soc.*, 1916, **38**, 2027—2038).—The various arsenates of lead have been prepared and studied, and a number of the earlier preparations have been critically discussed. The authors have prepared and described lead dihydrogen orthoarsenate, $PbH_4(AsO_4)_2$; lead hydrogen orthoarsenate, $PbH(AsO_4)$; lead orthoarsenate, $Pb_3(AsO_4)_2$; lead metarsenate, $Pb(AsO_3)_2$; lead dihydrogen pyroarsenate, $PbH_2As_2O_7$; and lead pyroarsenate, $Pb_2As_2O_7$. *Lead dihydrogen orthoarsenate* is prepared by adding lead hydrogen orthoarsenate to a boiling solution of arsenic acid of strength greater than 86%. The product is better if about 2% of nitric acid is added to the arsenic acid solution. It crystallises in long, narrow, rhomboidal plates. These are negative biaxial and extinguish at an angle of 8° to the longer edge. The minimum index of refraction is 1·75, and they are strongly birefringent. D_{15}^{15} 4·46. It is decomposed by water into lead hydrogen orthoarsenate and arsenic acid. On heating at 150°, approximately one-half of the constitutional water is lost, the residue being driven off just below a red heat. *Lead hydrogen orthoarsenate* is precipitated as a bulky, amorphous powder by adding a fairly concentrated solution of lead nitrate to a solution of disodium hydrogen arsenate. On dissolving this powder in nitric acid and keeping the solution under a bell-jar in the neighbourhood of a soluton of ammonia, thin, monoclinic leaflets crystallise out. These have a high birefringence and extinguish at 29°. The crystals have D_{15}^{15} 6·053 and the amorphous powder D_{15}^{15} 5·93. *Lead*

orthoarsenate was prepared by fusing a mixture of lead hydrogen orthoarsenate and litharge in the theoretical proportions in a blowpipe flame. An irregular, twinned mass was obtained of positive character, with low birefringence and D^{15} 7·32. *Lead metarsenate* was produced by fusing arsenic acid with the requisite quantity of litharge. It crystallises in hexagonal plates which have a very low birefringence and D 6·42. It is readily decomposed by water,, giving dilead orthoarsenate and arsenic lead. *Lead dihydrogen pyroarsenate*.—This compound is presumably formed when lead dihydrogen orthoarsenate is heated at 150° for seven hours. *Lead pyroarsenate* is prepared by heating dilead orthoarsenate at about 300°. It melts in the blowpipe flame, and cools to form a yellow, crystalline mass. The crystals are positive biaxial and have D 6·85.

J. F. S.

Basic Copper Sulphates. S. W. Young and Allen Edwin Stearn (*J. Amer. Chem. Soc.*, 1916, **38**, 1947—1953).—A series of experiments undertaken with the object of ascertaining the cause of the varying composition of the mineral brochantite. The formation of basic sulphates of copper has been studied by shaking solutions of copper sulphate with amounts of copper oxide varying from one-fourth to 8 molecules per molecule of copper sulphate. The experiments were carried out at 25°, 37·5°, and 50°. When equilibrium had been reached, the solutions were filtered, and both filtrate and precipitate analysed. It is shown that at 25° equilibrium is set up in three months, whilst at 50° two weeks is required. Other things being constant, the composition of the basic sulphates is independent of the temperature of preparation within the range investigated. It is highly probable that the solid basic substances obtained are not definite compounds, but are to be regarded rather as a three-component system in which all three components ($CuSO_4$, CuO, H_2O) are continuously variable within certain limits. It is shown that the maximum number of molecules of copper oxide which may be taken up by one molecule of copper sulphate is two, and that the formula for the most basic salt is probably $CuSO_4,2CuO,2H_2O$. In salts of lower basicity, the water content of the salt increases as the copper oxide content decreases, but there is no evidence to show that this change is maintained up to $CuSO_4,5H_2O$. Heating copper sulphate and water together in varying relative amounts does not lead to the formation of a definite basic copper sulphate, as has been maintained by many observers. The experiments indicate the existence of a series of metastable sulphates. The whole of the experiments go to show that it is to be expected that the mineral brochantite should show a variable composition depending on the conditions of its formation. J. F. S.

Oxidation of Manganous to Manganic Salts by Nitrous Acid. William Prandtl (*Ber.*, 1916, **49**, 1613—1614).—If a drop or two of a manganous salt solution is added to a cold solution of sodium nitrite in concentrated hydrochloric acid, there develops a

deep brownish-yellow coloration, due to the manganic chloride which is formed. Similarly, if oxalic acid is added to a solution of sodium nitrite containing a mere trace of a manganous salt, the deep cherry-red colour of manganic oxalate appears. J. C. W.

The Influence of Carbon and Manganese on the Corrosion of Steel. Sir ROBERT HADFIELD and J. NEWTON FRIEND (*J. Iron Steel Inst.*, 1916, **93**, 48—76).—The corrodibility of steels containing less than 0·2% of manganese in tap-water or sea-water increases with the carbon content. The attack by 0·5% sulphuric acid also increases with the carbon, reaching a maximum at the eutectoid composition and then falling. Steels containing about 0·7% Mn behave in a similar manner, but the rate of attack by acid is very much greater than in the case of steels containing less manganese. With manganese from 2 to 16%, the corrodibility in neutral solutions is greatly diminished, especially with high carbon, but the attack by acid is greatly accelerated. C. H. D.

Theory of the Corrosion of Steel. LESLIE AITCHISON (*J. Iron Steel Inst.*, 1916, **93**, 77—101).—The carbides in steels are not attacked during corrosion, but act as cathodes. The more finely divided the carbides, the greater is their action in accelerating corrosion. In pure ferrite, which also corrodes, the electrochemical difference may be attributed to the presence of an amorphous, intercrystalline layer. The results of measurements of the corrosion of alloy steels (T., 1915, **107**, 1531; this vol., ii, 37) show that the protective influence of an alloying metal on ferrite does not become appreciable until a fairly large percentage of the added metal is present. In the corrosion of pearlite, only the ferrite is dissolved, the fine particles of cementite disappearing through mechanical action. C. H. D.

Initial Temperature and Cooling Velocities of a Chromium Steel. C. A. EDWARDS, J. N. GREENWOOD, and H. KIKKAWA (*J. Iron Steel Inst.*, 1916, **93**, 114—154).—The steel used for the experiments contained C 0·63, Si 0·07, Mn 0·17, and Cr 6·15%. Such a steel is self-hardening, the self-hardening property depending on the rate of cooling. The critical cooling velocity which produces hardening diminishes as the initial temperature is raised. The hardened steel contains much martensite, and when the carbide change has been entirely suppressed, and the steel is purely martensitic, the hardness is a maximum. The critical cooling rates for a chromium steel are very much slower than the corresponding rates for a carbon steel, but the mechanism of the change is the same. It is possible that the carbide, Cr_3C_2, first passes into solution as a double molecule, Cr_6C_4, and dissociates as the temperature is raised. On cooling, the association only takes place slowly, and the more complete the dissociation the more readily is the carbide change suppressed. C. H. D.

Gases Occluded in Alloy Steels. J. W. DONALDSON (*Iron Steel Inst. Carnegie Scholarship Mem.*, 1916, **7**, 41—54).—Steels containing about 3% of nickel, silicon, chromium, and manganese

evolve gas when heated in a vacuum, the quantity diminishing in the order given. The nature of the gases is similar to that from ordinary carbon steels, carbon monoxide predominating at high, and hydrogen at low, temperatures. Silicon and manganese decrease the quantity of carbon monoxide relatively to hydrogen. Most of the gas is evolved in the neighbourhood of the critical points. C. H. D.

The Oxygen Content of Iron and Steel. J. ALLEN PICKARD (*Iron Steel Inst. Carnegie Scholarship Mem.*, 1916, **7**, 68—82).—Analyses of blown Bessemer metal and of iron which had remained under a highly oxidising slag for many hours in a basic open-hearth furnace show that the solubility of ferrous oxide in molten iron amounts to about 0·405% FeO. Microscopical evidence seems to show that a considerable part of this remains in solid solution. Oxygen in greater quantity than 0·01% is probably harmful to steel, although ingot iron practically free from carbon is not brittle even with much larger proportions of oxygen. The carbon monoxide and dioxide extracted from steel by heating in a vacuum are probably not present as such, but are formed by the action of the carbide on oxide in the metal. Whilst grey cast iron is almost free from oxygen, an appreciable quantity is found in white cast iron, and this may be due to the trapping of carbon monoxide during chilling. C. H. D.

The Relative Merits of Various Agents for the Deoxidation of Steel. H. M. BOYLSTON (*Iron Steel Inst. Carnegie Scholarship Mem.*, 1916, **7**, 102—171).—The effects of titanium, manganese, silicon, and aluminium on the properties of steel have been examined. There is no definite relation between the quantity of gas given off by a steel when heated in a vacuum and the soundness of the steel. There is no great difference in the influence of the different deoxidisers, and when separate properties of the steel are considered, the order of effectiveness of the different deoxidisers is not the same. C. H. D.

Preservation of Iron and Steel by Means of Passivifying Factors. THOMAS G. THOMPSON (*Iron Steel Inst. Carnegie Scholarship Mem.*, 1916, **7**, 232—298).—The corrosion of iron and steel in solutions of salts is greatly retarded by the addition of potassium dichromate. Disodium hydrogen phosphate also retards corrosion in salt solutions at the ordinary temperature, but does not render the metal passive. At high temperatures the phosphate, even in small quantities, accelerates corrosion, but the dichromate produces passivity even in boiling solution. The removal of zinc from galvanised iron by salt solutions is accelerated by dichromate. C. H. D.

Iron–Carbon–Silicon Alloys. J. H. ANDREW (*Iron Steel Inst. Carnegie Scholarship Mem.*, 1916, **7**, 1—17. Compare Gontermann, A., 1911, ii, 1091).—Alloys are prepared by melting together pig-

iron and ferro-silicon in crucibles. Quenching cast iron so as to obtain a white iron, and thus to increase the carbide, produces a double freezing point when the metal is re-melted, the upper point then corresponding with the separation of carbide, but equilibrium is restored on cooling. With 4·5% of silicon the pearlite point disappears altogether. The freezing point of the cast iron employed, containing 3·5—4·0% C, is raised at first by the addition of silicon and then depressed, the maximum occurring at about 3% Si. The $Ar_{3 \cdot 2}$ point is raised by silicon, and this may account for the insolubility of carbon in a high silicon alloy, the iron being in the α-state.

Pure eutectoid steel gradually deposits graphite when annealed for long periods at 600°, and this resolution of the carbide is accelerated by the presence of silicon. A double diagram for the iron–carbon system is suggested, one form representing the changes on heating and the other on cooling. C. H. D.

Colloidal Arsenates and Phosphates of Iron. HARRY N. HOLMES and R. E. RINDFUSZ (*J. Amer. Chem. Soc.*, 1916, **38**, 1970—1982).—A large number of experiments are described on the preparation of sols of ferric arsenates and phosphates, together with preliminary experiments on the corresponding salts of chromium and aluminium. The precipitated arsenates and phosphates of iron are gelatinous and difficult to wash free from adsorbed ions. They may be purified by repeated shaking with sand and a large volume of water, followed by decantation or filtration. Ferric orthoarsenate and orthophosphate may be peptised by relatively small amounts of ammonium hydroxide, yielding stable colloids. On long-continued dialysis these were found, contrary to the experience of Grimaux (*Compt. rend.*, 1884, **98**, 1540), to form deep red gels. The composition of both sol and gel of the arsenate corresponds closely with the formula $FeAsO_4,Fe_2O_3,xH_2O$. The change in composition from that of the precipitated arsenate and the formation of the final sol and gel are brought about by the removal of ammonium arsenate during dialysis. The same is true of the phosphate. The peptisation by ammonium hydroxide is probably due to the action of the hydroxyl ion, since with certain limitations other hydroxides and substituted ammonias may be used as peptising agents. The colloid formed by using an aqueous solution of methylamine yielded on dialysis a sol of deeper red colour than that formed in other cases. Both colloids have great adsorptive power, and carry into suspension with them other insoluble hydroxides on peptisation. Ammonium hydroxide also peptisises ferric pyrophosphate, ferric metaphosphate, and ferric arsenite. In the case of arsenates and phosphates of chromium and aluminium there appears to be very little peptisation. In the case of arsenates and phosphates of zinc and nickel, unstable sols are formed which settle out on dialysis. Ferric orthoarsenate and orthophosphate are peptised by solutions of ferric chloride, and yield on dialysis a red gel after removal of most of the chlorine ion. In the same way, similar salts of chromium and aluminium

form similar gels. The precipitated orthoarsenates and orthophosphates of any of the common metals are peptisised in ferric chloride solution, and on dialysis yield gels of ferric orthoarsenate and orthophosphate. If the ferric chloride is overloaded with the arsenate or phosphate, a butter-like mass is formed, which gives up its adsorbed ions very slowly. If a solution of a sulphate is used as the peptisising agent instead of a chloride, a sol is formed which is stable on keeping, but on dialysis completely separates out and forms a powdery mass. In all the cases of peptisation by salts the action is due to acid hydrolysis, as shown by the fact that hydrochloric and nitric acids may be used as peptisising agents with equally good results. The sols formed by acids give excellent gels on dialysis, but lighter in colour than those formed from ferric chloride solution. The action of sulphuric acid is the same as that of a sulphate. There are at least two kinds of peptisation of the ferric arsenates and phosphates: that by acids and that by bases. The formation of the sol and gel in the case of acid peptisation is due to the disturbance of the equilibrium by dialysis. This is shown by the fact that good gels may be formed by dialysing dilute mixtures of ferric chloride and arsenic or phosphoric acid. Ferric pyroarsenate, pyrophosphate, metaphosphate, and hypophosphite behave like the orthophosphates in peptisation by acids and ferric chlorides. J. F. S.

Electrolytic Preparation of Chromous Salts from Chromic Salts. Some New Salts of Bivalent Chromium. WILHELM TRAUBE and ALICE GOODSON (*Ber.*, 1916, **49**, 1679—1691).—The authors have made a quantitative study of the electrolytic reduction of chromic salts at a cathode of pure lead, measuring the amount of chromous salt produced at any given time by adding an excess of iodine and titrating the unused portion, or following the course of the reduction by readings at a voltameter and at the electrolytic cell of the volume of hydrogen liberated in a given time. To protect the solutions against the air, they were covered with light petroleum. It is found that the most favourable conditions for economical reduction are the electrolysis of the violet chromic salts in moderately acid concentrated solutions, with a current density of about 2·5 amperes per square decimetre. The more common green salts, in equivalent solutions, require a greater expenditure of current than the violet salts, but they yield much more concentrated solutions and are, therefore, more suitable in the end for the production, at any rate, of solutions rich in chromous salts but not entirely free from chromic salts. The same slower reduction of the green complexes is observed when solutions are treated with zinc.

A well-cooled concentrated solution of chromous chloride, prepared by electrolytic means, has been mixed with various alkali salts of organic salts, and the following new salts have been obtained: *chromous formate*, $CrX_2,2H_2O$, red cubes; *chromous ammonium formate*, NH_4CrX_3, pale brownish-red needles; red *chromous glycollate*, CrX_2,H_2O; Bordeaux-red *chromous malonate*,

$CrX,2H_2O$; blue *chromous sodium malonate*, $Na_2CrX_2,4H_2O$. These salts have the usual blue colour of chromous salts in solution.

J. C. W.

Behaviour of Chromous Salts towards Acetylene. Reducing Action of Salts of Bivalent Chromium. WILHELM TRAUBE and WILLIBALD PASSARGE (*Ber.*, 1916, **49**, 1692—1700).—Chromous salts are gradually oxidised, especially in acid solutions, with the liberation of hydrogen, thus: $2CrO + H_2O = Cr_2O_3 + H_2$. Because of this, they are able to reduce compounds with double or triple linkings in the presence of water, and examples of such reductions are now given.

Acetylene is reduced to ethylene, but not to ethane. Thus, on shaking 1200 c.c. of the gas with a solution of chromous chloride made by adding an excess of zinc to 70 grams of green chromic chloride dissolved in 120 c.c. of 25% hydrochloric acid, complete reduction to ethylene occurred in less than an hour. The possibility of preparing a chromous chloride solution readily by electrolytic reduction (see preceding abstract) increases the interest of this reaction.

Maleic and fumaric acids are readily reduced to succinic acid, both with acid and alkaline solutions of chromous chloride. Cinnamic and phenylpropiolic acids both yield β-phenylpropionic acid, but only with an alkaline suspension of the chromous oxide. Nitrous oxide is reduced in the presence of alkali hydroxides to nitrogen, nitric acid and hydroxylamine to ammonia, quantitatively. Nitrous acid, however, does not give a quantitative yield of ammonia.

Benzaldoxime is also readily transformed into benzylamine.

J. C. W.

Reactions of Non-aqueous Solvents. I. The Action of Chromyl Chloride on the Phosphorus Trihaloids. HARRY SHIPLEY FRY and JOSEPH L. DONNELLY (*J. Amer. Chem. Soc.*, 1916, **38**, 1923—1928).—The reactions between chromyl chloride and phosphorus trichloride and phosphorus tribromide have been carefully studied. It is shown that when small quantities of the two substances are brought together an explosive action takes place (compare Michaelis, *Jahresb. Chem.*, 1871, 248). The author has shown that the reactions may be moderated by bringing the substances together in 0·2 mol. solutions in dry carbon tetrachloride. The stoicheiometric relations in which these substances react has been determined by titrating a measured volume of the solution of chromyl chloride with a similar solution of phosphorus trichloride or tribromide, the end-point being determined by withdrawing a drop of the solution and mixing it with acetyl bromide on a glazed tile, when the presence of chromyl chloride is indicated by an intense violet-red coloration, due to the formation of chromyl bromide (Fry, A., 1911, ii, 610). In both cases it is shown that 2 molecules of chromyl chloride react with 3 molecules of the phosphorus haloid, the reactions being analogous:

$$2CrO_2Cl_2 + 3PCl_3 = 2(CrOCl{\cdot}POCl_3) + PCl_5.$$

These double compounds are solid and extremely deliquescent; the bromine compound is a purplish-grey powder. They react with water with the development of heat, according to the equation:

$$CrOCl \cdot POCl_3 + 2H_2O = CrCl_3 + HCl + H_3PO_4.$$

On ignition. compounds, CrOCl (or $Cr_2O_3,CrCl_3$) and CrOBr (or $Cr_2O_3,CrBr_3$), are produced. J. F. S.

Mineralogical Chemistry.

Chemical Structure of Natural Asphalte. J. MARCUSSON (*Zeitsch. angew. Chem.*, 1916, **29**, i, 346—348, 349—351).—A summary of the knowledge on this subject. T. H. P.

Alunite from Marysvale, Utah. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 150—151).—The occurrence of alunite near Marysvale has been described by B. S. Butler and H. S. Gale (*Bull. U.S. Geol. Survey*, 1912, **511**). Analysis I is of pink, translucent, coarsely granular, crystalline material, and II of compact, fine-grained material resembling porcelain:

	Al_2O_3.	Fe_2O_3.	K_2O.	Na_2O.	SO_3.	P_2O_5.	SiO_2.	H_2O at 105°.	H_2O >105°.	Total.
I.	37·18	trace	10·46	0·33	38·34	0·58	0·22	0·09	12·90	100·10
II.	34·40	trace	9·71	0·56	36·54	0·50	5·28	0·11	13·08	100·18

Analysis I of the more pure material agrees closely with the usual formula $3Al_2O_3,K_2O,4SO_3,6H_2O$. When ignited, the powdered mineral gives off all its water and three-fourths of its sulphuric acid (44%), the residue consisting of soluble potassium sulphate (18%) and alumina (37%). About 92% of the total potassium sulphate is thus extracted from the mineral by ignition and leaching. L. J. S.

Alunite, Psilomelanite, and Titanite. EDGAR T. WHERRY (*Proc. U.S. Nat. Museum*, 1916, **51**, 81—88).—A phosphate-bearing alunite from Gonzales County, Texas, is white (very slightly yellow), chalky, and compact. D 2·67, H $1\frac{1}{2}$, n 1·580±0·005. Analysis I, by J. E. Whitfield, corresponds with: 51·01% of the alunite molecule $K_2[Al(OH)_2]_6(SO_4)_4$, which is here called *kalioalunite*; 32·80% of the corresponding sodium compound, called *natroalunite*; 3·90% of the molecule $K_2H_4[Al(OH)_2]_6(PO_4)_4$, called *kaliohitchcockite*; 2·42% of *natrohitchcockite* (these representing end-members of the alunite–beudantite group, A., 1911, ii, 1101), and a residue of 9·96% of clay as impurity:

	Al_2O_3.	Fe_2O_3.	K_2O.	Na_2O.	SO_3.	P_2O_5	SiO_2.	H_2O.	Total.
I.	36·31	0·34	6·39	2·81	32·89	2·20	3·95	15·20	100·09
II.	39·02	—	3·05	5·27	30·52	—	7·46	14·87	100·19
III.	38·46	—	1·04	6·83	25·03	—	10·27	17·60	99·23

A sodium-bearing alunite from the Funeral Range Mountains, near Death Valley, California, is white, chalky, and compact. D 2·63, H $2\frac{1}{2}$—$3\frac{1}{2}$, n $1{\cdot}585 \pm 0{\cdot}005$. Analysis II of material from near the surface, and III of material from a depth of 60 feet, both by R. K. Bailey, corresponding respectively with 54·98 and 56·60% natroalunite with 21·82 and 5·90% kalioalunite, and remainder of 23·39 and 36·73% representing clayey impurities.

A lithium-bearing psilomelane from Tennessee, black and botryoidal, with D 4·20—4·30, gave analysis IV, by J. E. Whitfield. The barium may be present as sulphate and phosphate, the alumina and silica as clay, and the ferric oxide as limonite, whilst the other constituents are probably adsorbed in the manganese dioxide gel:

	H_2O.	Li_2O.	Na_2O.	K_2O.	CaO.	BaO.	MnO.	CoO.
IV.	11·40	0·35	1·20	0·44	trace	3·12	5·84	1·76

	NiO.	Al_2O_3.	Fe_2O_3.	MnO_2.	SiO_2.	P_2O_5.	SO_3.	Total.
IV.	0·32	7·83	2·20	56·54	7·68	0·49	0·89	100·06

Titanite of unusual habit occurs near Lambertville, New Jersey, as yellowish-brown, radiated-acicular crystals embedded in datolite. Analysis by J. E. Whitfield gave V:

	CaO.	Fe_2O_3.	TiO_2.	SiO_2.	P_2O_5.	Total.	Sp. gr.
V.	27·32	6·32	36·40	29·16	0·42	99·62	3·52

This corresponds with 89·21% of the titanite molecule, $CaTiSiO_5 = Ca(TiO)''SiO_4$, with a remainder of 10·41%, giving the ratios $Ca(FeO)'_2SiO_4$, suggesting a compound isomorphous with titanite. L. J. S.

Inyoite and Meyerhofferite. Two New Calcium Borates. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 35—55).—Large, rough, white crystals of rhombic habit from a colemanite deposit in the Mount Blanco district, Death Valley region, Inyo Co., California, were found to consist of a nucleus of colourless, glassy material (called *inyoite*, $2CaO,3B_2O_3,13H_2O$) surrounded by a reticulated or stellated mass of silky, fibrous material (called *meyerhofferite*, $2CaO,3B_2O_3,7H_2O$). The large crystals are thus pseudomorphs of meyerhofferite after inyoite, the alteration being due to loss of water on prolonged exposure to the air.

Approximate measurements of these pseudomorphous crystals show that inyoite is monoclinic with the axial ratios $a:b:c = 0{\cdot}94:1:0{\cdot}67$; $\beta = 62\frac{1}{2}°$. The glassy material shows a good cleavage parallel to the base $c(001)$. D 1·875, H about 2, refractive indices low, $\alpha = 1{\cdot}495$, $\beta = 1{\cdot}51$, $\gamma = 1{\cdot}520$. Before the blowpipe this material decrepitates and fuses with intumescence; it is readily soluble in acids. Analysis I agrees with the formula

$$2CaO,3B_2O_3,5H_2O + 8H_2O.$$

	CaO.	B_2O_3.	$H_2O(<110°)$.	$H_2O(>110°)$.	Total.
I.	20·5	[37·2]	26·1	16·2	100·0
II.	25·45	46·40	1·01	27·75	100·61
III.	25·6	[45·6]	0·3	28·5	100·0

The white, fibrous meyerhofferite gives place on the surface of the pseudomorphs to small, transparent, colourless, prismatic crystals

of the same material. These are triclinic ($a:b:c=0.7923:1:0.7750$; $\alpha=89°32'$, $\beta=78°19'$, $\gamma=86°52'$) with a perfect cleavage parallel to $b(010)$. D 2·120, H about 2, refractive indices: $\alpha=1.500$, $\beta=1.535$, $\gamma=1.560$. The material fuses without decrepitation, but with intumescence, to an opaque, white enamel; it is readily soluble in acids. II is the mean of three analyses of the opaque, white, fibrous material, and III an analysis of the colourless, transparent, prismatic crystals, both agreeing with the formula

$$2CaO,3B_2O_3,7H_2O.$$

These new minerals differ from colemanite ($2CaO,3B_2O_3,5H_2O$) in the amount of their water of crystallisation. Meyerhofferite as well as the enneahydrate ($2CaO,3B_2O_3,9H_2O$) of the same series were prepared artificially by Meyerhoffer and van't Hoff (A., 1907, ii, 260). L. J. S.

Spencerite, a New Zinc Phosphate from British Columbia. T. L. WALKER (*Min. Mag.*, 1916, **18**, 76—81).—The new mineral occurs as the core of stalactites of hemimorphite in the Hudson Bay zinc mine, near Salmo, in the West Kootenay district. It is snow-white, with brilliant pearly lustre on the perfect cleavage. The three rectangular cleavages and the optical characters suggest at first rhombic symmetry, but complex lamellar twinning is present, and etched figures are symmetrical about one plane only; the crystallisation is therefore probably monoclinic. The following mean of two analyses agrees closely with the formula

$$Zn_3(PO_4)_2,Zn(OH)_2,3H_2O.$$

ZnO.	P_2O_5.	H_2O (at 160°).	H_2O (above 200°).	Total.	Sp. gr.
60·18	26·18	9·81	3·50	99·67	3·143

The mineral differs from the basic zinc phosphate tarbuttite (A., 1908, ii, 397) in containing water of crystallisation.

L. J. S.

Lucinite, a New Mineral Dimorphous with Variscite. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 56—68).—This occurs in intimate association with variscite near Lucin, in Utah (A., 1911, ii, 1103). It forms minute, green crystals of octahedral habit; these are orthorhombic with $a:b:c=0.8729:1:0.9788$, and differ only slightly in angles (less than 1°) from the orthorhombic variscite, the crystals of which are tabular in habit with $a:b:c=0.8944:1:1.0919$. The refractive indices ($\alpha=1.56$, $\gamma=1.59$) are very slightly higher than those of variscite. Analysis I is of granular material underlying the octahedral crystals, and II of 25 mg. of material consisting largely of the octahedral crystals with some granular material and tabular crystals of variscite. These analyses agree with the variscite formula $Al_2O_3,P_2O_5,4H_2O$. All the water is lost below 180°.

	Al_2O_3.	P_2O_5.	H_2O.	SiO_2.	Total.	Sp. gr.
I.	34·97	42·75	22·75	[26·29 deducted]	100·47	2·52—2·53
II.	29	44	22	1	96	-

L. J. S.

The Amblygonite Group of Minerals: Fremontite (=Natramblygonite). W. T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 141—142).—Various objections having been raised against the name natramblygonite (A., 1911, ii, 121), the new name, *fremontite*, from Fremont Co., Colorado, is now proposed to take its place. The following, sometimes placed together under the species amblygonite, are reckoned as distinct mineral species: Amblygonite, $Li(AlF)PO_4$; montebrasite, $Li(AlOH)PO_4$; and fremontite, $Na(AlOH)PO_4$. Durangite, $Na(AlF)AsO_4$, belongs to the same group. L. J. S.

Schneebergite. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 81—94).—Schneebergite was first described by Brezina (A., 1882, 150) as a calcium antimonate occurring as transparent, honey-yellow octahedra. Later Eakle and Muthmann (A., 1895, ii, 512) asserted it to be identical with garnet. As a matter of fact, both these minerals, very similar to one another in external appearance, occur in association at Schneeberg, Saxony, together with calcite, breunnerite, magnetite, copper-pyrites, etc. The schneebergite crystals are cubic, showing only the form of regular octahedron. They show anomalous low birefringence, but become optically isotropic at a high temperature. Refractive index 2·09, D 5·41. The mineral is very difficultly fusible, and is insoluble in acids, but is decomposed in a sodium carbonate fusion. Analysis gave:

Sb.	O.	FeO.	CaO.	Na_2O.	Insol.	H_2O.	Total.
57·40	15·19	8·51	17·42	0·10	0·30	1·67	100·59

The water shown in this analysis was absorbed during the prolonged grinding to a fine powder; unground crystals yield no water. Oxygen was determined by reducing the mineral in a current of hydrogen and weighing the water, and its amount corresponds with the oxide Sb_2O_4. The simplest formula, $R''SbO_3$, or more exactly $Fe''Ca_3(SbO_3)_4$, is interpreted as a mixture of pyro-antimonate and pyro-antimonite, $2CaO,Sb_2O_5 + 2CaO,Sb_2O_3$. L. J. S.

Romeite. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 95—103).—The re-examination of schneebergite (see preceding abstract) led also to a re-examination of romeite and atopite. Romeite occurs at San Marcel, Piedmont, as thin veins between braunite and a mixture of piedmontite and albite. The small crystals are cubic octahedra with an imperfect octahedral cleavage. The colour of the crystals is russet, and of the powder seashell-pink. There is low anomalous double refraction; refractive index, 1·87. The mineral is infusible before the blowpipe, and is insoluble in acids. Analysis I corresponds with the formula $5R''O,3Sb_2O_5$; this may be regarded as a salt of a partly dehydrated pyro-antimonic acid, $3Sb_2O_5,6H_2O - H_2O = H_{10}Sb_6O_{20}$:

	Sb.	O.	FeO.	MnO.	CaO.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	56·15	18·57	1·12	6·27	15·81	0·81	1·39	100·12	5·074
II.	56·02	18·70	1·29	2·62	14·81	5·08	1·12	99·64	5·044

The original Swedish atopite was not available, but a re-examination of the so-called atopite from Miguel Burnier, Minas Geraes, Brazil (A., 1905, ii, 398), proves the identity of this with romeite. The characters are the same (refractive index 1·83), and analysis II agrees with the same formula. L. J. S.

The Natural Antimonites and Antimonates. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 104—105).—Six antimony acids are enumerated, namely, ortho-, pyro-, and meta-antimonous acids and ortho-, pyro-, and meta-antimonic acids, respectively $H_6Sb_2O_6$, $H_4Sb_2O_5$, $H_2Sb_2O_4$, and $H_6Sb_2O_8$, $H_4Sb_2O_7$, $H_2Sb_2O_6$. Hypo-antimonic acid, $H_2Sb_2O_8$, derived from the tetroxide, may be regarded as the salt antimonious ortho-antimonate, $Sb'''_2Sb^{V}_2O_8$. Sixteen mineral salts are listed and compared with corresponding arsenates, phosphates, vanadates, columbates, tantalates, nitrates, and titanates. L. J. S.

Koechlinite (Bismuth Molybdate), a New Mineral. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 10—34).—Greenish-yellow crystals having the form of thin, square plates at first thought to be torbernite, are present as a single specimen in the Natural History Museum at Vienna. The specimen came from the Daniel mine at Schneeberg, Saxony, and shows, in addition to koechlinite, native bismuth and some undetermined minerals on a matrix of quartz. The crystals are orthorhombic ($a:b:c=0·9774:1:1·0026$); they are tabular parallel to the macropinacoid $a(100)$, and have a perfect cleavage in this direction. Twinning on the brachydome (011) is frequent, and markings and etched figures on the faces suggest that the crystals may be hemimorphic. The refractive indices are very high, $\beta_{Li}=2·55$. The mineral fuses readily, and is readily soluble in hydrochloric acid, but not so easily in nitric acid. Deducting quartz, the average of three partial analyses made on small amounts of material is: Bi_2O_3, 77·1; MoO_3, 22·4; H_2O, 0·2%, corresponding with the formula Bi_2O_3,MoO_3, which may be written as $(BiO)'_2MoO_4$, bismuthyl molybdate. L. J. S.

Probable Identity of Mariposite and Alurgite. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 139—140).—A comparison of Hillebrand's analyses of mariposite (A., 1899, ii, 37) with Penfield's analysis of alurgite (A., 1894, ii, 55) suggests the identity of these minerals; and this is fully supported by a comparison of their physical and optical properties, so far as these have been determined. The alurgite analysis gives the formula $6(H,K)_2O,2MgO,3Al_2O_3,12SiO_2$, and the mariposite micas probably represent a mixture of this with a second end-member, the formula of which is perhaps $3H_2O,K_2O,4Al_2O_3,12SiO_2$. L. J. S.

The Chemical Composition of Tremolite. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 133—136).—Five trustworthy analyses of tremolite by Allen and Clement (*Amer. J.*

Sci., 1908, **26**, 101) showed about 2—2½% of water, which was expelled only at a high temperature; this they regarded as dissolved water held in solid solution, and not as an essential component of the mineral. A recalculation of these analyses shows that the ratio $RO:SiO_2$ approximates very closely to 1:1 when the water is included with the bases, but when it is neglected this ratio is 0·88:1. Water therefore enters into the composition of the mineral, and the formula is written $H_2O,2CaO,5MgO,8SiO_2$, instead of that usually given, namely, $CaO,3MgO,4SiO_2$. L. J. S.

Velardeñite, a New Member of the Melilite Group. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 106—108).—The compound $2CaO,Al_2O_3,SiO_2$ enters into the composition of the isomorphous series of melilite and gehlenite, and it has been prepared artificially by Weyberg (A., 1905, ii, 89) and by Shepherd and Rankin (A., 1911, ii, 725). The composition of the "gehlenite" from the Velardeña mining district, Mexico, described by Wright (A., 1909, ii, 61) can be explained by a mixture of 80% of this molecule with 20% of åkermanite, $4MgO,8CaO,9SiO_2$; and the physical characters of this mineral agree closely with those of the artificial compound, to which the name velardeñite is applied. In seventeen published analyses of members of the melilite series the velardeñite molecule enters into eleven, and in three of them to the extent of more than 50%. L. J. S.

The Melilite Group. WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1916, **610**, 109—128).—A review is given of the several attempts to explain the composition of the minerals: melilite, gehlenite, åkermanite, and fuggerite. They are now explained as isomorphous mixtures of the following four primary compounds: Sarcolite, $3CaO,Al_2O_3,3SiO_2$; a hypothetical soda-sarcolite,

$$3Na_2O,Al_2O_3,3SiO_2,$$

velardeñite, $2CaO,Al_2O_3,SiO_2$ (see preceding abstract); and åkermanite, $4MgO,8CaO,9SiO_2$. Seventeen published analyses are recalculated and found to accord with this theory. The greatest divergence is shown by those rich in iron, in which perhaps a ferric iron sarcolite, $3CaO,Fe_2O_3,3SiO_2$, may be present. The results are plotted on a triangular diagram (sarcolite and soda-sarcolite being here combined). The fact that the optical sign of these minerals varies from positive to negative suggests that the refractive indices are not linear functions of the chemical composition; or perhaps there may be a double compound of åkermanite and sarcolite.

L. J. S.

Sulphatic Cancrinite from Colorado. ESPER S. LARSEN and GEORGE STEIGER (*Amer. J. Sci.*, 1916, [iv], **42**, 332—334).—This mineral is a constituent of the rock uncompahgrite (A., 1914, ii, 813) from Beaver Creek, Gunnison Co., Colorado, having been apparently derived from melilite. It is colourless with a poor prismatic cleavage and rod-like inclusions parallel to the prismatic axis. It differs from ordinary cancrinite, optically, in its lower refractive

indices ($\omega = 1{\cdot}509$, $\epsilon = 1{\cdot}500$), and birefringence ($\omega - \epsilon = 0{\cdot}009$, positive); and, chemically, in containing much SO_4, isomorphously replacing CO_3. Analysis by G. Steiger gave:

SiO_2.	TiO_2.	Al_2O_3.	CaO.	SrO.	K_2O.	Na_2O.	H_2O at 105°.	H_2O.	CO_2.	SO_3.	Total.
33·70	0·07	29·40	4·18	0·08	1·45	18·52	0·72	4·24	3·18	4·65	100·19

L. J. S.

Optically Positive Cordierite. I. C. Chacko (*Geol. Mag.*, 1916, [vi], **3**, 462—464).—Violet patches and spots of cordierite are present in a diorite from Teruwulla, in Travancore. Under the microscope, the mineral shows strong pleochroism and lamellar twinning; numerous globular inclusions (the larger ones identified as monazite) are surrounded by pleochroic halos. The optic sign is sometimes negative, as is usual in cordierite, but sometimes it is positive, this being due to the fact that the optic axial angle 2V is near 90°. Analysis of material with D less than 2·65 gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
49·74	35·21	5·65	3·00	1·05	4·30	1·74	100·69

In this analysis ferric oxide has perhaps been estimated too high and the ferrous oxide too low. L. J. S.

Ceriferous Eucolite from Madagascar. A. Lacroix (*Bull. Soc. franç. Min.*, 1915, [that is, 1916], **38**, 278—285).—Fine-grained soda-granites occurring near Ampasibitika, north-west Madagascar, contain ægirite, riebeckite, zircon, and a mineral allied to eucolite. The last is yellowish-brown to rose, and forms small globular or rhombohedral crystals. It is optically uniaxial and negative, and strongly pleochroic. D 2·97. Material could not be separated for analysis, but the following results were obtained by Pisani on the portion of the rock decomposed by hydrochloric acid:

SiO_2.	ZrO_2.	$(Ce,La,Di)_2O_3$.	FeO.	MnO.	CaO.	Na_2O.	Total.
40·0	16·4	22·5	5·6	0·1	6·1	6·6	97·3

Analyses of the rocks show: SiO_2, 66·4—70·8; Na_2O, 5·1—7·3; Ce_2O_3, 0·40—1·30; ZrO_2, 0·65—3·71; etc. This type of rock is very similar to rockallite, but differs in containing eucolite, and it is named fasibitikite. L. J. S.

The Meteoric Stones of Launton, Warbreccan, Cronstad, Daniel's Kuil, Khairpur, and Soko-Banja. G. T. Prior (*Min. Mag.*, 1916, **18**, 1—25).—In this series of chondritic meteoric stones there is a wide range in the amounts of metallic nickel–iron present (4—25½%). The conclusion is drawn that in chondritic meteoric stones the less the amount of nickel-iron the richer it is in nickel, and the richer in iron are the associated magnesium silicates (see following abstract).

I. The Launton stone was seen to fall on February 15th, 1830, at Launton, near Bicester, Oxfordshire; its original weight was

1023 grams, and it has not previously been examined in detail. It belongs to the intermediate veined chondrite group. Under I is given the bulk-analysis deduced from the analyses of the portions attracted and unattracted by a weak magnet; I*a* gives the composition of the olivine ($3\cdot3Mg_2SiO_4,Fe_2SiO_4$) from an analysis of the portion of the unattracted material soluble in dilute hydrochloric acid; and I*b* gives the calculated mineral composition. II. The Warbreccan stones were found in 1904 in the Warbreccan run, about forty miles west of Windorah, in central Queensland. Two large stones weigh 31,610 and 29,100 grams (about 69 and 64 lb. respectively), and a third weighs 443 grams. They belong to the white-veined chondrite group. The composition (II*a*) of the olivine is $3\cdot37Mg_2SiO_4,Fe_2SiO_4$. III. The Cronstad (Orange

	Fe.	Ni.	Co.	Fe.	S.	Ca.	S.	SiO_2.	TiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.
I.	7·20	1·20	0·08	3·80	2·18	—	—	39·70	0·18	2·40	0·31	1·49
II.	6·03	1·06	0·08	4·09	2·31	—	—	39·86	0·21	1·71	0·41	2·15
III.	16·71	1·55	0·23	3·29	1·88	—	—	37·24	0·30	2·41	0·37	—
IV.	23·70	1·78	0·12	5·15	2·94	0·48	0·38	38·47	0·12	1·78	0·23	—
V.	16·83	1·29	0·17	4·47	2·56	0·19	0·15	42·64	nil.	1·76	†	2·88
VI.	3·17	1·06	0·09	3·17	1·81	—	—	41·45	0·10	2·12	0·36	—

	FeO.	MnO.	NiO.	CaO.	MgO.	K_2O.	Na_2O.	P_2O_5.	H_2O.	C.	Total.
I.	12·35	0·29	0·12	2·09	24·89	0·09	1·01	0·15	0·42	—	99·95
II.	12·84	0·39	0·12	2·01	24·75	0·06	0·92	0·26	0·80	—	100·06
III.	9·17	0·04	0·10	1·45	23·61	0·07	0·67	0·25	0·34	—	99·68
IV.	0·23	0·02	0·11	1·03	21·63	0·15	0·64	trace	0·34	0·32	99·91*
V.	—	—	—	1·46	23·09	0·10	0·80	trace	0·20	0·41	99·68†
VI.	17·73	0·05	—	1·92	25·63	0·07	0·85	0·24	0·17	—	99·99

* Including Cr_2S_3, 0·29. † Including FeO,Cr_2O_3, 0·39; FeS,Cr_2S_3, 0·29.

	SiO_2.	FeO.	CaO.	MgO.	FeS, etc.	Insol.	Total.
I*a*.	17·05	9·25	0·35	17·34	8·94	46·65	99·58
II*a*	16·60	9·62	—	18·09	10·53	44·68	99·52
III*a*.	14·85	7·49	—	16·36	6·63	54·78	100·11
VI*a*.	20·29	14·44	0·35	19·26	5·51	40·17	100·02

	Felspar.	Chromite.	Daubreelite.	Apatite.	Bronzite.	Olivine.	Oldhamite.	Troilite.
I*b*.	10·82	0·45	—	0·36	29·50	41·91	—	5·98
II*b*.	8·50	0·60	—	0·59	33·54	39·80	—	6·40
III*b*.	9·43	0·54	—	0·56	35·03	29·44	—	5·17
IV*b*.	8·47	0·34	0·40	—	55·76*	—	0·86	7·96
V*b*.	8·25	0·39	0·29	—	60·31*	—	0·34	7·03
VI*b*.	9·09	0·45	—	0·56	30·60	49·61	—	4·98

	Nickel-iron.	Graphite.	Water.	FeO,TiO_2.	Fe_2O_3.	NiO.	Total.	Sp. gr.
I*b*.	8·48	—	0·42	0·33	1·49	0·12	99·86	3·35
II*b*.	7·17	—	0·80	0·39	2·15	0·12	100·06	3·48
III*b*.	18·49	—	0·34	0·56	—	0·10	99·66	3·61
IV*b*.	25·45	0·32	0·34	0·36	—	—	100·26	3·66
V*b*.	18·29	0·41	0·20	—	2·88	—	99·90†	3·49
VI*b*.	4·32	—	0·17	0·18	—	—	99·96	—

* Enstatite. † Including SiO_2, 1·51.

Free State) stones fell on November 19th, 1877. They belong to the grey chondrite group. The composition (III*a*) of the olivine

is $4Mg_2SiO_4,Fe_2SiO_4$. IV. The Daniel's Kuil (Griqualand West, South Africa) stone fell on March 20th, 1868; its original weight was 2 lb. 5 oz. It was partly analysed by A. H. Church (this Journal, 1869, **7**, 22). V. The Khairpur (Punjab, India) stones fell on September 23rd, 1873. This and Daniel's Kuil belong to the rare Hvittis type of meteoric stones. VI. The Soko-Banja (Alexinatz, Serbia) stones fell on October 13th, 1877; VI gives the bulk-analysis, VI*a* the composition of the olivine, $2\frac{1}{2}Mg_2SiO_4,Fe_2SiO_4$, and VI*b* the mineral composition.

L. J. S.

The Genetic Relationship and Classification of Meteorites. G. T. Prior (*Min. Mag.*, 1916, **18**, 26—44).—Chondritic meteoric stones are divided into four groups, of which the following are taken as the types: (1) Daniel's Kuil (Hvittis); (2) Cronstad; (3) Baroti (A., 1914, ii, 64); and (4) Soko-Banja. The conclusion arrived at from the analyses of these stones (see preceding abstract) is illustrated in the following table:

Type.	Percentage of nickel-iron.	Ratio of Fe to Ni in nickel-iron.	Ratio of MgO to FeO in olivine.	Ratio of MgO to FeO in pyroxene.	Ratio of total Fe atoms to Mg atoms.
(1) Daniel's Kuil ...	$25\frac{1}{2}$	13	—	∞	1·03
(2) Cronstad	$18\frac{1}{2}$	11	4	6	1·22
(3) Baroti	9	$6\frac{1}{2}$	3	4	1·46
(4) Soko-Banja	4	3	$2\frac{1}{2}$	3	1·80

These groups, depending on the richness in nickel of the nickel-iron and its interrelation with the ratio of MgO to FeO in the magnesium silicates, are given the symbols C1—C4. In the same way, non-chondritic stones (achondrites) fall into four groups, A1—A4, with an extra group, A5, for the angrites, nakhlites, etc., and the meteoric irons (siderites) into the groups S1—S4.

It is supposed that all meteorites have been derived from a single magma, the differences between them depending on the degree of oxidation. With increasing amount of oxygen, the smaller amount of the metallic portion becomes richer in nickel and the magnesium silicates richer in iron. L. J. S.

Amount of Phosphoric Acid in the Sea-water of Plymouth Sound. Donald J. Matthews (*Reprint. J. Marine Biol. Assoc. United Kingdom*, 1916, **11**, 122—130).—From September, 1915, to February, 1916, the average amount of phosphoric acid (P_2O_5) in water collected half a mile outside Plymouth breakwater was 0·044 mg. per litre; an increase in the amount was noticed when the supply of land-water rose after rain. It was found that, although previous oxidation with permanganate considerably increased the quantity of phosphoric acid, oxidation by boiling with permanganate was not complete. The method adopted for the estimation consisted in precipitating the phosphoric acid together with ferric hydroxide, dissolving the precipitate in nitric

acid, and then estimating the phosphoric acid colorimetrically as described by Pouget and Chouchak (A., 1909, ii, 266).

W. P. S.

Analytical Chemistry.

New Forms of Laboratory Apparatus. C. KIPPENBERGER (*Zeitsch. angew. Chem.*, 1916, **29**, i, 351—352, 359—360. Compare A., 1905, ii, 608).—Descriptions and views are given of: Three forms of apparatus for the treatment of a solid substance with cooled extracting solvent; in one form the solvent, after acting on the substance, passes into a purifier containing, for instance, either sulphuric acid to retain bases or a decolorising agent, and thence through a condenser to the bottom of the flask, from which the solvent is distilled. A perforator, which permits of the extraction of an aqueous liquid by a solvent heavier than water. A suction apparatus shaped like a jacketed funnel, the jacket being fitted with a short glass tube for connexion with a pump, and the inner surface ground to fit a small glass beaker; the base of the latter is blown in and perforated, and filled with asbestos sufficiently thickly to cover the perforations; the apparatus may be used, for example, for starch estimations, the starch being dried and weighed in the perforated beaker. A mechanical mixing apparatus for the estimation of milk-fat and other purposes. T. H. P.

The Estimation of the Relative Turbidity or Opacity of Fluid Suspensions including Bacterial Emulsions. GEORGES DREYER and ARTHUR DUNCAN GARDNER (*Biochem. J.*, 1916, **10**, 399—407).—A method is given for determining the relative turbidity of fluids placed in small test-tubes against a dark background by the use of artificial light, and its application to the measurement of agglutination of bacteria is described. S. B. S.

Volumetric Estimation of Hydrogen by Oxidation with Activated Chlorate Solutions. Removal of Carbon Monoxide by Means of Mercuric Chromate. K. A. HOFMANN (*Ber.*, 1916, **49**, 1650—1662. Compare this vol., ii, 45).—The oxidation of hydrogen in the sodium chlorate pipette for the purpose of gas analysis requires that both the hydrogen and the chlorate shall be activated. Palladium alone is not suitable for the first purpose, since it becomes oxidised by a chlorate in the presence of osmium tetroxide. For this reason, then, the porous tubes impregnated with platinum are used; the hydrogen is sufficiently quickly activated by the platinum to reduce the palladium oxide, and then the liberated palladium increases the activity. The activation of hydrogen is favoured in alkaline solutions, that of the chlorate by acids, wherefore a compromise is effected by using sodium hydrogen carbonate. Some new details are given about the preparation of a

pipette active enough to absorb hydrogen from rich gaseous mixtures within half an hour.

The velocity of the absorption by this pipette is so greatly lessened by traces of carbon monoxide that it is easy to recognise whether this gas has been incompletely removed from a mixture. The usual cuprous chloride reagents seldom effect a complete absorption of carbon monoxide. The last traces can be removed, however, by using a second pipette containing mercuric chromate deposited on broken earthenware, and the subsequent absorption of hydrogen then proceeds quickly. J. C. W.

Contact Poisons. Retardation of the Oxidation of Hydrogen in the Chlorate Pipette by Carbon Monoxide. K. A. Hofmann and Helge Schibsted (*Ber.*, 1916, **49**, 1663—1669. Compare preceding abstract).—Some experiments on the influence of carbon monoxide on the absorption of hydrogen in the chlorate pipette are reproduced by curves. Although carbon monoxide is itself oxidised, as little as 0·2% makes a pronounced effect on the absorption of hydrogen. This is not due to a mechanical poisoning of the hydrogen activator (palladium–platinum), but to a chemical effect on the activation of the chlorate solution, for an increase in the amount of the active oxidising agent, brought about by adding gaseous oxygen, accelerates the absorption. The pipette rights itself within an hour after being used for hydrogen and carbon monoxide mixtures if the platinised porous tubes are kept immersed in the chlorate solution. J. C. W.

Efficiency of Calcium Chloride, Sodium Hydroxide, and Potassium Hydroxide as Drying Agents. Gregory P. Baxter and Howard W. Starkweather (*J. Amer. Chem. Soc.*, 1916, **38**, 2038—2041).—The relative and the absolute efficiency of calcium chloride, sodium hydroxide, and potassium hydroxide as desiccating agents have been examined at 0°, 25°, and 50°. The various substances were dried by melting, broken into small pieces, and filled into two U-tubes so that a layer of 70 cm. was produced. Moist air was passed over this layer and then through a weighed tube of phosphoric oxide. A second series of experiments was also made in which dry air was passed over the system. From the results, it is shown that the lowest hydrate of calcium chloride has a maximum vapour pressure of 0·07 mm. at 0°, 0·34 mm. at 25°, and 1·34 mm. at 50°; sodium hydroxide, 0·04 mm. at 0°, 0·15 mm. at 25°, and 1·15 mm. at 50°; potassium hydroxide, 0·007 mm. at 50° The weight of water left in one litre of gas at 25° which has been dried by the following desiccating agents is: calcium chloride, 0·36 mg.; calcium bromide, 0·2 mg.; zinc bromide, 1·1 mg.; zinc chloride, 0·8 mg.; sodium hydroxide, 0·16 mg.; potassium hydroxide, 0·002 mg.; potassium hydroxide at 50°, 0·007 mg., and sulphuric acid, 0·003 mg. J. F. S.

Systematic Separation of the Anions of Group I. Anions the Silver Salts of which are Insoluble in Nitric Acid. H. C. P. Weber and H. A. Winkelmann (*J. Amer. Chem. Soc.*, 1916, **38**, 2000—2013).—A method is described by means of which any mix-

ture of the ions Cl', Br', I', CN', CNS',$Fe(CN)_6'''$, $Fe(CN)_6''''$, and S'' may be separated with quantitative accuracy. The separation is adequate when the respective ions form 0·01—0·0001 of the total. The method consists of six different stages: (1) The mixed solution is treated with 1—3 c.c. of dilute nitric acid and an excess of zinc nitrate solution, whereby the ferricyanide and ferrocyanide are precipitated. The precipitate is filtered and washed with dilute ammonium nitrate, and dissolved in 10 c.c. of 3% sodium hydroxide solution. To the resulting solution 5 c.c. of 5% ammonium nitrate and a few drops of zinc nitrate are added, when zinc ferrocyanide is precipitated, which may be confirmed by converting into cupric or ferric ferrocyanide. The ferricyanide is detected in the filtrate from the ferrocyanide by treating with dilute hydrochloric acid and a few drops of potassium iodide and 1 c.c. of chloroform, when the liberation of iodine indicates the presence of ferricyanide. (2) The filtrate from the zinc precipitation is treated with silver nitrate, filtered, and washed with very dilute nitric acid. (3) The precipitated silver salts are transferred to a beaker and treated with 2 c.c. of 2*M* mercuric acetate containing 5% acetic acid. The mixture is digested for fifteen minutes on a steam-bath, treated with 2 c.c. of 2*M* sodium acetate, and diluted to 20 c.c. The cyanide has been converted into a soluble mercuric complex, whilst the other silver salts are not attacked. The solution is filtered and treated with hydrogen sulphide to remove the mercury. This is filtered and treated with a little sodium hydroxide and a few drops of ammonium sulphide, and evaporated to dryness on a steam-bath. A little dilute sulphuric acid is added to decompose the excess of polysulphides, and after filtration, a little ferric chloride is added, when the formation of a blood-red coloration indicates the presence of cyanide in the original mixture. (4) The residual silver salts are treated with 10—15 c.c. of 8% sodium hydroxide and 1 gram of sodium formate, and boiled for five to ten minutes. The solution is made up to 20 c.c. and filtered, when the chloride and thiocyanate pass through as sodium salts, the residual silver salts remaining in the precipitate along with reduced silver. The solution is nearly neutralised with dilute sulphuric acid, and then treated with excess of sulphurous acid and copper sulphate solution. The precipitated cuprous thiocyanate is filtered off and the filtrate boiled with a little nitric acid to remove the sulphur dioxide, and treated with silver nitrate, when the chloride is precipitated. (5) The remaining precipitate from (4) is covered with concentrated ammonia, and a quantity of molecular copper is added, when the silver bromide and iodide are instantaneously reduced, and cuprous iodide and bromide pass into solution, leaving the silver sulphide unattacked. This is filtered off and the solution neutralised with sulphurous acid, and an excess of sulphuric acid is added. If iodide is present, there is a white precipitate of cuprous iodide. This is filtered off, and the filtrate warmed with nitric acid to remove the sulphur dioxide, and the bromide is precipitated by silver nitrate. (6) The precipitate, which contains any sulphide that may be present, is dissolved in

nitric acid diluted to 100 c.c., and precipitated as barium sulphate. The quantities mentioned in the above refer to an initial quantity of material of about 0·3 gram. A large number of analyses are quoted to show the trustworthiness of the separations. J. F. S.

Silver Chromate. P. N. VAN ECK (*Pharm. Weekblad*, 1916, **53**, 1554—1558).—In Mohr's method of estimating chlorides, the operation should be carried out at the ordinary temperature. The nitrate produced in the reaction has no appreciable influence on the silver chromate formed. A concentrated solution of ammonium nitrate is a good crystallising medium for silver chromate. A. J. W.

[Estimation of] Chlorides in the Presence of Thiocyanates. F. W. BRUCKMILLER (*J. Amer. Chem. Soc.*, 1916, **38**, 1953—1955). —It is shown that chlorides can be titrated with silver nitrate solution, using chromate as indicator, in the presence of thiocyanates. The method is applicable to the estimation of chlorides in water analysis. A sample is raised to the boiling point and nitric acid is added drop by drop, the amount required depending on the quantity of thiocyanate present. Generally, 2—3 c.c. are sufficient. The solution is boiled for fifteen minutes, and filtered if much sulphur is deposited. After cooling, it is neutralised with a normal solution of sodium hydrogen carbonate, using methyl-orange as indicator, and then titrated with silver nitrate in the usual way. Four points are specially investigated, with the following results: (1) It is shown that the thiocyanate may be decomposed at 100° by such quantities of nitric acid as are insufficient to oxidise or cause the vaporisation of the hydrochloric acid; (2) that all but traces of the hydrogen cyanide formed during the decomposition can be volatilised during the time required for oxidation; (3) that sulphur is not present in the oxidised solution in such a form as to react with the silver nitrate; and (4) that the colour of the methyl-orange indicator does not interfere with the chromate end-point. Incidentally, it is shown that chloride may be titrated in solutions containing 0·0007*N*-sulphuric acid, but above this concentration an end-point cannot be obtained. J. F. S.

Estimation of the Active Chlorine Content of Hypochlorites. COMTE (*J. Pharm. Chim.*, 1916, [vii], **14**, 232—233).—The iodometric method is recommended. The results obtained may be expressed in French chlorometric degrees, that is, litres of active chlorine per kilogram of the hypochlorite. W. P. S.

The Use of Methylene-blue as a Reagent in Chemical Analysis. Application of the Process to the Detection and Estimation of Perchlorates in Chili Saltpetre. A. MONNIER (*Arch. Sci. phys. nat.*, 1916, [iv], **42**, 210—216).—The following acids in dilute solutions, preferably in the form of their alkali salts, give coloured, crystalline precipitates with a solution of

methylene-blue. Hydriodic acid gives a deep blue precipitate, showing bronze-green by reflection; perchloric and hydroferricyanic acids, violet precipitates, bronze-green by reflection; persulphuric, dichromic, and permanganic acids, rose-violet precipitates, bronze-green by reflection; metavanadic, molybdic, and tungstic acids, deep blue precipitates. The precipitate with a persulphate is readily distinguished from that with a perchlorate in that the former when calcined leaves a slight residue showing the reactions of a sulphate, and the latter when heated decomposes violently with deflagration.

The amount of potassium perchlorate can be readily estimated colorimetrically in a sample of Chile saltpetre by this method. To 20 c.c. of a 5% solution of the crude nitrate 1 c.c. of a 0·3% solution of methylene-blue in water is added, and the mixture left overnight. A crystalline precipitate forms, and the supernatant liquid is tinted blue. This colour is compared with that of standard tubes containing varying amounts of pure potassium perchlorate. If the perchlorate is present to the extent of less than 0·2%, a 10% solution of crude nitrate, and if more than 0·5%, a 2·5% solution of crude nitrate is used. If the crude nitrate contains any iodide, this can be first removed by shaking the solution with moist silver oxide.

W. G.

Estimation of Hydrogen Sulphide in Water. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1916, **29**, i, 383—384).—The sample of water is taken in a 500 c.c. bottle containing from 10 to 20 grams of marble previously treated with dilute hydrochloric acid and washed; it should be ascertained that the marble yields carbon dioxide free from any trace of hydrogen sulphide. The bottle is filled completely with the water. Immediately before the estimation is commenced, the stopper of the bottle is removed and replaced by a rubber stopper, through which passes the stem of a bulb tube provided with a side-tube; a tapped funnel containing hydrochloric acid is attached to the top of the bulb tube, and the side-tube is connected with an absorption vessel containing acid-free bromine water. A small **U**-tube filled with cotton wool is placed between the side-tube and the absorption vessel. Hydrochloric acid is introduced slowly into the water in the bottle, and the carbon dioxide liberated from the marble passes over into the absorption vessel, carrying with it the hydrogen sulphide. The addition of the hydrochloric acid is so regulated that the evolution of carbon dioxide proceeds steadily for three hours. After this time, the contents of the absorption vessel are transferred to a basin, evaporated until all free bromine and hydrogen bromide have been expelled, and the solution then titrated with $N/100$-borax solution, using methyl-orange as indicator. Each c.c. of $N/100$-borax solution is equivalent to 0·1705 mg. of hydrogen sulphide. Since the oxidation of the hydrogen sulphide proceeds according to the equation $H_2S + 4Br_2 + 4H_2O = H_2SO_4 + 8HBr$, an alternative volumetric method may be used; the solution is boiled in a flask for ten minutes to expel free bromine, then cooled, and

titrated with $N/10$-borax solution. In this case, 1 c.c. of $N/10$-borax solution (19·11 grams of the crystallised salt per litre) corresponds with 0·341 mg. of hydrogen sulphide.

The following method is recommended for the estimation of hydrogen sulphide in relatively strong solution. A stoppered 250 c.c. flask containing 100 c.c. of $N/10$-permanganate solution and 1 gram of pure sodium hydroxide, is weighed. A few c.c. of the hydrogen sulphide solution are then introduced, and the flask is again weighed. After one hour, the contents of the flask are acidified with sulphuric acid, potassium iodide is added, and the liberated iodine titrated with $N/10$-thiosulphate solution. Each c.c. of $N/10$-permanganate solution is equivalent to 0·4263 mg. of hydrogen sulphide. W. P. S.

Micro-volumetric Analysis. II. Quantitative Estimation of Slight Quantities of SO_4.* H. J. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1916, **19**, 115—125).—The micro-volumetric method, already applied in the estimation of small quantities of potassium (this vol., ii, 50), has been found to yield satisfactory results in the estimation of sulphate by precipitation as barium sulphate. The precipitate is forced into a calibrated capillary tube by centrifuging, and when constant the volume of the precipitate is read off. The tube is calibrated by preliminary experiments with solutions containing known quantities of sulphate.

These experiments showed that the volume of a given quantity of precipitated barium sulphate depends on the size and shape of the crystals, and on this account it has been found necessary to carry out the precipitation under certain definite conditions. In particular, it is essential that the precipitated barium sulphate should consist of very small crystals, and this result may be attained by the addition of acetone.

The procedure adopted is to add 2·5 c.c. of hydrochloric acid (concentrated acid diluted with an equal volume of water) to 5 c.c. of the sulphate solution; to this solution are added 5 c.c. of a barium chloride solution (2·44% $BaCl_2,2H_2O$) containing three to five drops of acetone. The precipitate formed is centrifuged until the volume is constant.

When the estimation is carried out in this manner, the result obtained is not affected by the presence of sodium, potassium, calcium, magnesium, chloride, or phosphate in the original solution. H. M. D.

Detection of Small Quantities of Selenium and its Distinction from Arsenic. JEAN MEUNIER (*Compt. rend.*, 1916, **163**, 332—334).—Selenious acid and selenites in solution are reduced by nascent hydrogen, giving hydrogen selenide, which when heated decomposes, depositing selenium, this occurring if selenium is present when applying Marsh's test for arsenic. If there is a large amount of selenium present, it is readily detected by its red colour, but if the amount is very small, the deposit resembles that

* and *Biochem. Zeitsch*, 1916, **77**, 168—188.

of arsenic. The following process can be used to detect the selenium. A current of hydrogen sulphide is passed into the hot solution containing a little sulphurous acid. The precipitate of finely divided sulphur carries down with it any selenium and arsenious sulphide, and is clotted by stirring. If selenium is present, the clots are brown, whereas with arsenious sulphide they are yellow, as is the case with sulphur alone. The brown clots may be dried and the sulphur and selenium separated by careful sublimation in a closed tube. W. G.

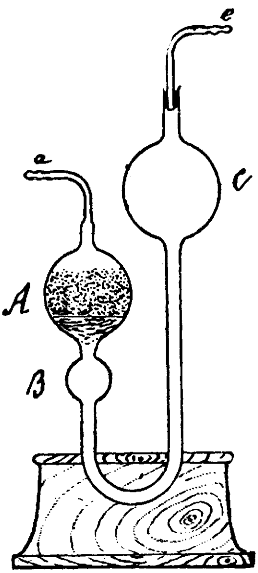
Weighing Boats for Kjeldahl Nitrogen Estimations. C. BAUMANN and J. GROSSFELD (*Chem. Zeit.*, 1916, **40**, 792).—For weighing soft or sticky materials, such as meat and jams, and for transferring them to the Kjeldahl decomposition flask, small boats of stout parchment paper are recommended. They are very light, contain only inappreciable quantities of nitrogen, and are readily and completely destroyed by the sulphuric acid during the combustion. G. F. M.

Estimation of Nitrogen in Organic Compounds by the Microchemical Method and by the Ordinary Method. G. FISCEMAN (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1915, [iii], **21**, 135—142).—The author suggests several modifications in Pregl's apparatus for the micro-estimation of nitrogen in organic compounds and in the method of using it (compare Dubsky, A., 1914, ii, 486).

The foaming which occurs in the 50% potassium hydroxide solution with which the micro-nitrometer is filled may be avoided by employing a 25% solution which has been subjected to protracted boiling; in this the bubbles of gas break readily.

When a Kipp's apparatus is used for generating the carbon dioxide, the air cannot be eliminated completely, even by boiling the liquid and the lumps of marble, and cooling in a current of carbon dioxide. Dubsky's empirical correction of the volume of nitrogen measured by diminishing it in all cases by 2% cannot be accepted. The inaccuracy of the measured volume of nitrogen is due partly to adhesion of the potassium hydroxide to the glass, which may cause a constant error, but the amount of air in the carbon dioxide is variable, and in the author's experiments is about 0·0015 c.c. per minute or 0·015—0·022 c.c. for a combustion lasting ten to fifteen minutes; this error, on a total gas volume of 0·5 c.c., represents 3—4%, and may be obviated by use of an apparatus devised by the author. It consists (see figure) of a bulb *A* fitted with a perforated base which is covered with glass-wool pressed moderately tightly; this serves as a holder for the calcium carbonate. The bulb *B*, the U-tube, and the bulb *C* serve as the acid reservoir. The apparatus is first filled with boiling water by applying suction at *e* by means of a pump, *a* being then closed and the suction increased in intensity, so that the water boils in the apparatus and is most drawn towards *e*. Boiling 50% potassium hydroxide solution is then sucked into the apparatus, *a* again closed,

and the suction increased, this operation being repeated two or three times. Boiling dilute hydrochloric acid and afterwards boiling water are similarly drawn into the apparatus, the tube *a* being subsequently connected by means of rubber tubing to a dish containing boiling water with finely divided marble in suspension, this having been previously boiled for at least an hour; in this way about one-half of the bulb *A* is filled with the powdered marble. Boiling dilute hydrochloric acid is then drawn in to such an extent that generation of carbon dioxide frees the bulb *A* and at least two-thirds of *B* from liquid. The tube *e* is detached from the pump and one-half of the water siphoned from *C* and replaced by concentrated hydrochloric acid. The tube *e* is then connected with the gas-delivery tube of an ordinary Kipp's apparatus for carbon dioxide, and *a* is joined, through a small washing bulb charged with concentrated sulphuric acid, to the combustion tube. With this arrangement the error due to air passing into the nitrometer is reduced to 0·08—0·12%. If the marble is suspected of being impure, a little permanganate may be added to the liquid in the bulb apparatus.



For each combustion 300 c.c. of carbon dioxide are more than sufficient, and the above generator with bulbs of 200—300 c.c. capacity yields enough gas for more than one hundred combustions; with larger bulbs (1—2 litres) the apparatus is applicable to macro-combustions.

In the author's experiments the error due to adhesion of the potassium hydroxide solution to the walls of the nitrometer amounts to 0·7%, so that the reading of the volume of gas must be diminished by 0·8%.

The Kuhlmann balance is accurate to 0·005—0·006 mg., but a less sensitive instrument would suffice.

Test combustions of *p*-nitrobenzaldehyde and azobenzene by the micro- and the ordinary macro-method show that the former gives the more exact results and occupies only forty-five to fifty minutes, whereas the latter method requires two and a-quarter to two and a-half hours. T. H. P.

Aeration Method for Ammonia. B. S. Davisson, E. R. Allen, and B. M. Stubblefield (*J. Ind. Eng. Chem.*, 1916, **8**, 896—899. Compare A., 1915, ii, 277).—This method, proposed originally by Folin (A., 1913, ii, 239), is trustworthy when the ammonia is liberated by magnesium oxide and an efficient absorption apparatus is employed. Large quantities of ammonia may be removed from 250 c.c. of solution within two and a-half hours if 1080 litres

of air per hour are used. Attention is called to the necessity of measuring the actual volume of air which passes through the apparatus, as this differs from that which a pump will deliver when working with no load. W. P. S.

Nitrates and Oxygen Demand (in Sewages). F. W. Bruckmiller (*J. Ind. Eng. Chem.*, 1916, **8**, 899—900).—The estimation of the oxygen requirement of sewages depends on the oxygen value ascribed to the nitrogen in the nitrate radicle. Of the values which have been proposed, the weight of evidence seems to be in favour of the assumption that 1 atom of nitrate nitrogen is equivalent to 2·5 atoms of oxygen. This value is not, however, applicable to all sewages, and for each different sewage the oxygen equivalent of the nitrate nitrogen should be estimated experimentally. This is best done by making parallel estimations, using nitrate in one and oxygen in the other as oxidising agents. W. P. S.

Detection of Phosphorus by the Method of Dusart and Blondlot, and its Application in Toxicology. H. J. Lemkes (*Pharm. Weekblad*, 1916, **53**, 1496—1513).—The author has investigated Dusart and Blondlot's method of detecting phosphorus, and found it satisfactory. A. J. W.

Does Vanadium Interfere with the Estimation of Phosphorus in Soils when the Phosphorus is Weighed as Magnesium Pyrophosphate? Ross Aiken Gortner and William M. Shaw (*Soil Sci.*, 1916, **2**, 299—304).—Estimation of phosphorus in soil solutions to which known amounts of vanadium were added showed that the vanadium has no appreciable effect on the results, either when the phosphorus is weighed as pyrophosphate or when the titrimetric method is employed. N. H. J. M.

Estimation of the Total Phosphoric Acid in Spodium. Ferdinand Pilz (*Chem. Zentr.*, 1916, i, 1268—1269; from *Zeitsch. landw. Vers.-Wesen Öster.*, **19**, 57—61).—Five grams of the spodium are heated for about five minutes in a platinum or quartz dish, and the pale grey mass is introduced into a dry 500 c.c. flask and boiled for thirty minutes with 50 c.c. of concentrated sulphuric acid and 5 c.c. of concentrated nitric acid. When cold, the liquid is diluted to the mark, mixed, and filtered, and 50 c.c. of the filtrate are treated with 100 c.c. of citrate solution and 50 c.c. of magnesia mixture. The liquid is filtered the next day through a Gooch crucible and the precipitate treated as usual. T. H. P.

Estimation of Silica in Soils. Béla von Horváth (*Zeitsch. anal. Chem.*, 1916, **55**, 513—536).—Results of a critical examination of methods for the estimation of amorphous silica in soils which have been extracted previously with hydrochloric acid, showed that in no case could trustworthy results be obtained. This was due to the use of different substances (alkalis, alkali carbonates, diethylamine, etc.) for dissolving the silica, and to

differences in the time of extraction, temperature, stirring, fineness of the soil, etc. The manner in which the soil had been treated with hydrochloric acid also affected the results obtained, which, for one soil, varied from 4·39% to 11·08% of silica. The alkali solutions are also capable of decomposing certain silicates, and it is suggested that they should be replaced by some more suitable solvent for silica; possibly one of the amines would serve this purpose. W. P. S.

Estimation of Carbon and Hydrogen by the Microchemical Method. G. Fisceman (*Rend. Acad. Sci. Fis. Mat. Napoli*, 1916, [iii], **22**, 31—38).—Modifications are made in Pregl's method (compare Dubsky, A., 1914, ii, 486). It is found that those substances which are most difficultly combustible burn readily when mixed with copper oxide, there being no need for the platinum boat or the "contact star" (compare Dennstedt, A., 1903, ii, 103, etc.); although the mixing occupies some little time, the amount of moisture absorbed from the air by the cupric oxide is without influence on the results. The calcium chloride apparatus consists, in place of a straight tube, of a U-tube 4 mm. in diameter and of a total length of 20 cm.

With Pregl's apparatus for absorbing carbon dioxide, the water-vapour emitted from the potassium hydroxide solution with which the glass-wool is moistened makes the first layer of calcium chloride wet, and thus completely obstructs the tube after one or at most two combustions; such obstruction may, indeed, occur during the course of a combustion. The apparatus used by the author consists of two parts: (1) a small glass gas-washing bottle which contains 30% potassium hydroxide solution and has two enlargements blown on its exit tube, these being filled with glass-wool; this exit tube is connected to (2), a tube 15 cm. long and 4 mm. in diameter, filled in its first part with soda lime and in the latter part with calcium chloride. The progress of the combustion may be followed by observation of the bubbles of gas passing through the potassium hydroxide solution in this apparatus.

If the copper block surrounding the part of the combustion tube corresponding with the lead peroxide is heated by the micro-burner, there is danger of the rubber connexion being heated and yielding volatile products, whereas if it is not heated, water-vapour may condense at the joint and thus escape absorption. This difficulty is obviated as follows: The copper block is heated gently (not above 150°), so that no condensation occurs in the lead peroxide and the subsequent rubber joint is not unduly heated. At the end of the combustion, the last calcium chloride tube and the carbon dioxide absorption apparatus are removed and the extremity of the calcium chloride U-tube is connected with a suction pump. The oxygen supply is discontinued, the whole apparatus evacuated, the connexion with the pump shut, and the tap of the oxygen cylinder reopened; the current of gas at reduced pressure readily evaporates any condensed water which is absorbed by the calcium chloride tube. When equilibrium is reached throughout

the apparatus, the gas current is maintained for a few minutes and the calcium chloride U-tube then detached and weighed.

The sole advantage of the micro-estimation of carbon and hydrogen lies in the small amount of the substance required. The combustion, including the weighings, occupies two and a-half to three hours and requires more attention than is the case with macro-combustion. T. H. P.

The Estimation of Free Carbon Dioxide in Water at its Place of Origin. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1916, **29**, i, 335).—The titration method of von Trillich as modified by the author (A., 1915, ii, 281) is further modified in order to enable estimations of carbonic acid in natural waters to be carried out at their place of origin, in that the titration is carried out in the sampling flask and the volume of standard sodium carbonate solution employed is read off on graduations in the neck of the flask. The latter is graduated at 100 c.c., 101 c.c., and thence in tenths of a c.c. to 105 c.c., and in order to obviate the necessity of shaking with the attendant loss of carbon dioxide, the mixing is carried out by using both phenolphthalein solutions and carbonate solutions of density considerably greater than that of the water, and giving the flask merely a rotary motion. The first object is achieved by adding an equal volume of glycerol to the alcoholic phenolphthalein solution and making the standard carbonate solution in a 10% solution of pure sodium sulphate. Both these solutions are carried in dropping bottles. G. F. M.

The Copper Sulphate Test for the Detection of Free Carbon Dioxide (in Water). L. W. WINKLER (*Zeitsch. angew. Chem.*, 1916, **29**, i, 366—367. Compare A., 1915, ii, 795).—Further experiments with this test showed that it is useful as a preliminary test, especially in the case of waters in which the temporary hardness lies between 2° and 20° (German). If the temporary hardness of a water is known, the time required for the production of a turbidity with the copper sulphate test affords an indication of the approximate quantity of free carbon dioxide present. The alizarin test (*loc. cit.*) is more suitable for use with very soft waters. W. P. S.

A Method for the Detection of Calcium in the Presence of Strontium and Barium. P. N. RAIKOW (*Chem. Zeit.*, 1916, **40**, 781).—Calcium may be directly detected in presence of strontium and barium by utilising the fact that its carbonate alone suffers decomposition when heated in an open porcelain dish with a Teclu burner. Accordingly, if 0·5—1·0 gram of the well-washed alkaline earth carbonates is heated thus for some minutes and the cooled product is stirred with water, a deep red colour will be imparted to phenolphthalein in the presence of calcium, but strontium and barium carbonates, not being decomposed into the oxides, give no such colour. As little as 0·002 gram of calcium carbonate in 1 gram of alkaline earth carbonates can be detected by this method. At

the temperature of the blowpipe flame all the carbonates suffer at least partial decomposition, and temperatures higher than that given by the Teclu burner must therefore be avoided. G. F. M.

Estimation of Calcium in the Ash of Forage Plants and Animal Carcases. S. B. KUZIRIAN (*J. Amer. Chem. Soc.*, 1916, **38**, 1996—2000).—A rapid and accurate method is described for the estimation of calcium in agricultural products. It consists essentially in the removal of phosphorus as ammonium phosphomolybdate from an acid solution of the ash and precipitation of the calcium from the filtrate as calcium oxalate, either directly or after the removal of the excess molybdenum as sulphide. Since no advantage is obtained by the removal of the molybdenum, it is recommended that this step be omitted. This method is compared with the basic acetate method, and shown to be superior to it in the following points: (1) The results are more accurate and concordant; (2) no attention need be given to the maintenance of exact neutrality of the solution; (3) the volume of the filtrate resulting from the precipitation of the phosphorus can be kept reasonably small, so that no evaporation is required; (4) the time required for a determination is much less; and (5) both calcium and phosphorus can be determined in the same solution. J. F. S.

A New Method for the Quantitative Estimation of Cadmium by Means of Pyridine. SIEGFRIED KRAGEN (*Monatsh.*, 1916, **37**, 391—408).—A method is described in which the cadmium is precipitated from chloride containing solutions as $CdCl_2,2C_5H_5N$. The dipyridine compound loses a molecule of pyridine when heated at 115—120°, but the monopyridine compound is quite stable even at 130—140°, and may be employed in the gravimetric estimation of the cadmium. The dipyridine compound is moderately soluble in pyridine, less in water, still less in alcohol, and only very slightly so in ethyl ether. The solubility in water is reduced by the addition of alkali chlorides, and to facilitate the precipitation of the cadmium, sodium chloride is added to the solution in considerable quantity.

A volumetric method is also described in which the precipitated dipyridine compound is dissolved in a measured volume of standard hydrochloric acid, the solution then saturated with sodium chloride, and the excess of acid estimated by titration with standard alkali, for which process patent-blue has been found to be the most suitable indicator.

Cupric chloride also forms a dipyridine compound, but this is much more soluble than the cadmium compound in pyridine solutions. This fact may be utilised in the qualitative separation of cadmium and copper, and also for the approximate estimation of the cadmium in the mixed solution. H. M. D.

Rapid Method for the Estimation of Manganese [in Steel] ERNST SZÁSZ (*Chem. Zeit.*, 1916, **40**, 810—811).—For the rapid estimation of manganese in steel, etc., the author recommends

Meineke's old method, which, although apparently complicated, exhibits the following advantages: (1) result obtained in twelve to fifteen minutes; (2) the presence of other metals, with the one exception of cobalt, is without influence on the results; (3) 2 grams of the sample is sufficient; and (4) the end-point is extremely sharp and permits of the use of artificial light. The author's modification of this method is carried out as follows.

The solutions required are: (1) 150 c.c. nitric acid (D 1·4), 50 c.c. concentrated sulphuric acid, and 400 c.c. of water; (2) 50 grams crystallised chromic acid dissolved in 100 c.c. of water; (3) 125 grams of zinc oxide are ground with 450 c.c. of cold saturated barium chloride solution and made up to 1 litre with water: both reagents should be indifferent towards permanganate; (4) zinc oxide is added in small portions to hydrochloric acid (D 1·12) until a small deposit remains undissolved in the boiling liquid; the solution, still kept boiling, is rendered pink by addition of permanganate, left twenty-four hours, and filtered through a thick filter; (5) hydrochloric acid, D 1·12; (6) standard permanganate solution containing about 2 grams of the salt per litre, 1 c.c. corresponding roughly with 0·001 gram of manganese; (7) 3 grams of antimony trioxide are dissolved in 250 c.c. of hydrochloric acid (D 1·12), and the solution made up to 1 litre; 3 c.c. of this correspond approximately with 2 c.c. of the permanganate solution. The procedure is as follows.

If the steel is difficultly soluble in nitric acid, 2 grams of it are first treated with 22·5 c.c. of a mixture of 25 c.c. of concentrated sulphuric acid and 200 c.c. of water, 7·5 c.c. of nitric acid (D 1·4) being added only after complete solution. With an ordinary steel or pig-iron, 2 grams are dissolved in a 500 c.c. measuring flask in 30 c.c. of solution (1) by heating on a gauze, the solution being boiled for a minute with 2 c.c. of chromic acid solution (2); 200 c.c. of cold water are then added, and the liquid cooled under the tap. One hundred c.c. of the well-shaken barium chloride–zinc oxide emulsion (3) are then added from a measuring cylinder, and the liquid is thoroughly mixed and quickly cooled, made up to the mark, mixed again, and filtered through a 32 cm. pleated filter (Schleicher and Schüll, No 588) into a 250 c.c. measuring flask (=1 gram of sample).

Meanwhile, into another 500 c.c. measuring flask, 20 c.c. of zinc chloride solution (4) and sufficient of the standard permanganate to give an excess of at least 1 c.c., or, better, 1—3 c.c., have been introduced. The 250 c.c. of filtered solution (see above) are then run into this permanganate solution, which is kept moving so that there is an excess of permanganate throughout the liquid. The liquid is made up to the 500 c.c. mark, mixed, and filtered through a 24 cm. pleated filter (Schleicher and Schüll, No. 588) into the 250 c.c. flask previously used; this flask is rinsed out three times with the first portions of about 30—50 c.c. each of the filtrate, and the filter is kept as full as possible with the liquid. The 250 c.c. of filtrate (=0·5 gram of sample) are poured into a vessel containing 30 c.c. of hydrochloric acid (D 1·12) and rather more of the

antimonious chloride solution (7) than is necessary to decolorise the excess of permanganate; the colourless liquid obtained is then titrated with permanganate.

The use of filter paper necessitates the introduction of an empirical paper-coefficient which, with the above conditions, amounts to 0·3, 0·4, 0·5, 0·6, and 0·7 c.c. of permanganate when the excess of the latter is 1, 2, 3, 4, and 5 c.c. respectively. These values are obtained by analysing a steel of exactly known manganese-content, using different excesses of the permanganate solution. The same normal steel may be used to standardise the permanganate solution, but the filtrations must then be made through asbestos, so as to render the results independent of the paper-coefficient.

Example: Suppose that 5 c.c. of antimonious chloride solution, corresponding with 3·15 c.c. of permanganate, were taken and the liquid is titrated back with 1·80 c.c. of the permanganate. The excess of the latter will be $3·15 - 1·80 = 1·35$ c.c. per 0·5 gram, or 2·70 c.c. per 1 gram of the sample. The corresponding paper-coefficient being 0·47 c.c., the total excess of the permanganate is 3·17 c.c. If 7 c.c. of permanganate were added, the volume used will be $7·0 - 3·17 = 3·83$ c.c., and the percentage of manganese in the sample will be $3·83 \times 100 \times$ titre of the permanganate solution.

T. H. P.

Volumetric Method for the Estimation of Cobalt. W. D. ENGLE and R. G. GUSTAVSON (*J. Ind. Eng. Chem.*, 1916, **8**, 901—902).—The method proposed depends on the fact that cobalt is oxidised by treatment with a perborate in alkaline solution, whilst nickel is not affected; the oxidation may also be made with hydrogen peroxide, but a perborate is preferable, since the excess used is more readily destroyed than is hydrogen peroxide. The solution containing cobalt, nickel, zinc, and alkalis, but free from heavy metals, iron, manganese, and any substance which will liberate iodine from potassium iodide, is acidified with a slight excess of sulphuric acid, 2 grams of sodium perborate are added, the mixture is then rendered strongly alkaline with sodium hydroxide, boiled for ten minutes to decompose the excess of perborate, cooled to the ordinary temperature, treated with 1 gram of potassium iodide, then acidified with dilute sulphuric acid, and the liberated iodine titrated with thiosulphate solution. The latter solution may be standardised against a pure cobalt compound, or, if this is not available, against potassium dichromate; 1 mol. of dichromate is equivalent to 6 atoms of cobalt.

W. P. S.

A Colorimetric Method for the Estimation of Acetylene. ARMIN SCHULZE (*Zeitsch. angew. Chem.*, 1916, **29**, i, 341—342. Compare Weaver, this vol., ii, 275).—Acetylene was estimated colorimetrically by comparing with standard tints the red colour produced in ammoniacal cuprous solutions, to which a little gelatin had been added to prevent coagulation of the colloidal cuprous acetylide. The cuprous solutions were prepared by dis-

solving 0·75 gram of cupric chloride in water, adding 1·5 grams of ammonium chloride, 3 c.c. of 20% ammonia, 2·5 grams of hydroxylamine hydrochloride, and finally 6 c.c. of 2—3% gelatin solution, and making up to 50 c.c. with water. The solution should be freshly prepared, and 5 c.c. were taken for each estimation in a test-tube, a measured quantity of the acetylene mixture being bubbled through. The colours produced were permanent for about three days. The method was also used for the estimation of acetylene in aqueous solution, but the sensitiveness appeared to be less in this case, and another series of standards must therefore be used. In a gaseous mixture, as little as 0·001 c.c. of acetylene could be detected. G. F. M.

Hydrolysis of Ethyl Sulphuric Acid and the Assay of Aromatic Sulphuric Acid, U.S.P. W. B. D. PENNIMAN, W. W. RANDALL, C. O. MILLER, and L. H. ENSLOW (*J. Ind. Eng. Chem.*, 1916, **8**, 904—908).—Ethyl sulphuric acid is not hydrolysed to any appreciable extent by cold water even after a considerable length of time, but hydrolysis takes place slowly when the mixture is boiled under a reflux apparatus. The decomposition of the acid is, however, never complete, and for this reason the U.S. Pharmacopœia method for the analysis of aromatic sulphuric acid always gives low results. If the alcohol resulting from the hydrolysis is removed as soon as it is formed, the reaction proceeds to completion. For the estimation of total sulphuric acid in aromatic sulphuric acid it is therefore recommended that a portion of the sample be mixed with water and heated in an open beaker, which is placed in a boiling water-bath; after four hours' heating the reaction is completed, and the mixture is then titrated with standard alkali solution. Attention is directed to the fact that alkali ethyl sulphates are hydrolysed to little, if any, extent when heated with the addition of water. W. P. S.

The Estimation of Phenol in the Crude Phenols from Coal Tar. RENÉ MASSE and HENRI LEROUX (*Compt. rend.*, 1916, **163**, 361—363).—The method is a slight modification of that usually employed for the estimation of phenol in the crude distillates, and is based on the solidification curve for mixtures of phenol and the mixed cresols containing not more than 33% of the cresols. W. G.

Separate Estimation of Cholesterol and Cholesterol Esters in Small Amounts of Blood. W. R. BLOOR and ARTHUR KNUDSON (*J. Biol. Chem.*, 1916, **27**, 107—112).—The method consists in (*a*) the estimation of the total cholesterol in an aliquot portion of an alcohol–ether extract of blood by the process previously described (this vol., ii, 275), and (*b*) the estimation of cholesterol esters in another aliquot portion after removal of the free cholesterol by precipitation with digitonin. The cholesterol esters are separated from the digitonin precipitate by repeated extraction with light

petroleum (b. p. 40—60°). The difference between (*a*) and (*b*) represents free cholesterol.

Free cholesterol constitutes from 30 to 40% of the total cholesterol in normal human blood-plasma. H. W. B.

Fundamental Analytical Methods in Sugar Chemistry. EMILE SAILLARD (*Mon. Sci.*, 1916, [v], **6**, 194—203, 224—228).—A survey of the analytical methods used in the sugar industry in France, certain of the methods being criticised and in some cases alternate methods suggested (compare A., 1915, ii, 71, 290; this vol., ii, 55). W. G.

Estimation of Pentose or Pentosans by Means of Fehling's Solution. JULIAN L. BAKER and H. F. E. HULTON (*Analyst*, 1916, **41**, 294—297).—Eynon and Lane's modification of Flohil's method (compare A., 1912, ii, 305) for the estimation of furfuraldehyde, obtained from pentosans by distillation with hydrochloric acid, was investigated by the authors. They confirm the values found by Eynon and Lane for the furfuraldehyde–copper ratio, but find that somewhat larger quantities of cuprous oxide are produced by the action of sodium chloride on Fehling's solution than were given by Eynon and Lane. The acidity of the distillate obtained in the estimation should be estimated by titration of an aliquot portion in order to ascertain the proportion of sodium chloride present in the portion of the neutralised distillate used for the copper reduction. It is recommended that a larger volume than 20 c.c. of Fehling's solution should be used with a proportionately larger quantity of the distillate in order to increase the weight of cupric oxide obtained and thus reduce the error. Instead of boiling the mixture of distillate and Fehling's solution over a flame, the flask containing the mixture should be immersed in a boiling water-bath for thirty-five minutes; in this way the amount of cuprous oxide produced by the sodium chloride is diminished considerably (to 4 mg. per 10 grams of sodium chloride), whilst the furfuraldehyde–copper ratio is not affected. W. P. S.

Saccharimetric Normal Weight and Specific Rotation of Dextrose. RICHARD F. JACKSON (*J. Washington Acad. Sci.*, 1916, **6**, 530—531).—Pure dextrose containing 1 molecule of water of crystallisation was dehydrated at 60—80° and used in the following experiments. The density of aqueous solutions of dextrose were determined at 20° and shown to agree with the expression $D_{4^\circ}^{20^\circ} = 0{\cdot}99840 + 0{\cdot}003788p + 0{\cdot}00001412p^2$, where p is the percentage of anhydrous dextrose by weight in a vacuum. The formula holds for values of p between 5 and 30. Twelve determinations were made to ascertain the quantity of dextrose, dissolved in 100 c.c. of solution, which would cause a rotation of 100° S on the scale of a quartz wedge saccharimeter. If the saccharimeter is controlled by the conversion factors found by Bates and Jackson, or by the rotation of sucrose, the normal weight of dextrose is 32·231 grams (vacuum standard with brass weights); if the saccharimeter is calibrated by the Herzfeld-Schönrock factor the value is 32·264

grams. The rotations are not strictly proportional for concentrations less than the normal, and a series of correcting factors from 90° S to 10° S is given. The rotation of the normal solution for $\lambda = 5461$ Å. is 40·898°. The specific rotation of dextrose corresponds with the formulæ $[\alpha]^{20°}_{5461A} = 62{\cdot}032 + 0{\cdot}04257c$, where c is the weight of anhydrous dextrose in 100 c.c. of solution (vacuum standard), and $[\alpha]^{20°}_{5461A} = 62{\cdot}032 + 0{\cdot}04220p + 0{\cdot}0001897p^2$, where p is the percentage of dextrose by weight in the solution. J. F. S.

Methods for Estimation of Four or More Carbohydrates Involving Oxidation with Bromine. EDITH GERTRUDE WILSON and WILLIAM RINGROSE GELSTON ATKINS (*Biochem. J.*, 1916, **10**, 504—521).—An attempt has been made to estimate lævulose in the presence of maltose and dextrose by treatment of a solution of these sugars with bromine water at the ordinary temperature for sixty hours, which should oxidise maltose and dextrose, and leave lævulose intact. It was found, however, that maltose and dextrose, when submitted to this treatment, showed a slight residual reducing power to Fehling's solution, and that lævulose also underwent a slight oxidation. Nevertheless, moderately accurate estimations of lævulose in the presence of the other sugars could be made by this method. For analysis, then, of a mixture of sucrose, maltose, lævulose, and dextrose, the following operations can be carried out: (*a*) The amount of sucrose is estimated by polarisation and reduction before and after treatment with invertase. (*b*) The lævulose is then estimated by oxidation with bromine water under standard conditions (in presence of $N/10$-sulphuric acid at the ordinary temperature, etc.). (*c*) The rotations due to lævulose and sucrose are allowed for in the original solution. (*d*) The reduction due to lævulose is subtracted from the initial reduction, and this gives the reduction due to dextrose and maltose. From these data, equations can be constructed to give the amounts of the various sugars. Attempts were also made to estimate the amounts of sugars in solutions of mixtures by investigating the rate of change in their reducing powers when kept in alkaline solutions, and to use Barfoed's reagent quantitatively. They led, however, to no successful method. S. B. S.

A Method for the Estimation of Free and Combined Galactose. A. W. VAN DER HAAR (*Chem. Weekblad*, 1916, **13**, 1204—1213).—Free galactose, either alone or mixed with other sugars, and combined galactose in galactosides, can be estimated by oxidation with nitric acid to pyromucic acid. A. J. W.

Method for the Detection of Arachidic Acid. ROBERT H. KERR (*J. Ind. Eng. Chem.*, 1916, **8**, 904).—As little as 5% of earthnut oil may be detected in other oils by means of the following method for the isolation of the arachidic acid occurring in earthnut oil. Twenty grams of the oil under examination are saponified by boiling with 200 c.c. of 95% alcohol and 10 c.c. of 50% aqueous potassium hydroxide solution; the mixture is then neutralised with

alcoholic acetic acid solution (50 c.c. of glacial acetic acid in 150 c.c. of 95% alcohol), and boiled after the addition of 50 c.c. of magnesium acetate solution (10 grams of magnesium acetate, 100 c.c. of water, and 100 c.c. of 95% alcohol). The mixture is now cooled, kept at 15° for about eighteen hours, the precipitate then collected on a filter, washed twice with 50% alcohol and three times with water, and next decomposed by mixing it with hot water and adding sulphuric acid. The layer of fatty acids is separated, washed with hot water, dissolved in 100 c.c. of 90% alcohol, and the arachidic acid obtained from this solution by crystallisation. W. P. S.

Detection of Benzoic Acids in Fats. W. STADLIN (*Chem. Zeit.*, 1916, **40**, 770).—The isolation of small quantities of benzoic acid from fats is more conveniently carried out by dialysis than by extraction. Twenty to 30 grams of the fat in a semi-fluid condition are placed in the parchment diaphragm of a dialyser and covered with 50% alcohol. The outer compartment is filled with alcohol of the same strength, and dialysis is allowed to proceed for twenty-four hours. The dialysate is then rendered faintly alkaline and evaporated on the water-bath, the alcohol being replaced by water, and the aqueous liquid acidified and extracted with ether. The residue from the ether extract is then tested for benzoic acid by oxidation to salicylic acid by the Jonescu and Fleury method, namely, by the addition of 3 drops each of ferric chloride solution, hydrogen peroxide solution, and ferrous sulphate solution, when a violet colour appearing in about thirty seconds indicates the initial presence of benzoic acid. Salicylic acid must obviously be tested for previously in the dialysate by means of ferric chloride.
G. F. M.

Detection of Acetone in the Urine. O. SAMMET (*Chem. Zentr.*, 1916, ii, 33—34; from *Schweiz. Apoth.-Zeit.*, 1916, **54**, 77—80, 89—91).—The author examines every sample of urine received as soon as possible by Légal's or Kraft's ring test and by Frommer's method for the presence of acetone. If both tests give an undoubtedly negative result, this is accepted. In all doubtful cases and with urines to be examined specially for acetone and also with diabetic urines which have been found previously to contain acetone, the urine is distilled and the distillate tested for acetone by the above methods. Frommer's test (*Berlin Klin. Woch.*, **42**, 1005) is based on the formation of di-*o*-hydroxydistyryl ketone or its red alkali salts. Ten c.c. of the urine are heated to 70° with about 1 gram of solid potassium hydroxide and 10 drops of salicylaldehyde; in presence of acetone, an intense cherry-red or purplish-red ring forms in the lower part of the test-tube. This test is extremely delicate and definite, but a pale pink or orange-red ring must not be regarded as indicating acetone.

In estimating acetone in urine by the method proposed by Messenger (A., 1908, ii, 234; compare Sammet, A., 1913, ii, 449), tartaric or oxalic acid (2—3 grams per 100 c.c.) should be used for the

acidification of the urine in place of the acetic acid originally suggested; further, the concentration of the sugar in the distillation flask should not be too high, so that diabetic urines should be diluted with an equal volume of water before distillation, and not more than one-half of this diluted urine should be distilled.

T. H. P.

Colorimetric Method for the Estimation of Acetone in Urine. FRANK A. CSONKA (*J. Biol. Chem.*, 1916, **27**, 209—212).—The method is based on the red colour of the alkaline salt of di-*o*-hydroxydistyryl ketone, which is produced when acetone is treated with salicylaldehyde in the presence of potassium hydroxide. If the urine is free from sugar, it is rendered alkaline with a few drops of potassium hydroxide solution, filtered, and salicylaldehyde and excess of potassium hydroxide added directly to the filtrate. Acetoacetic acid does not react with salicylaldehyde in alkaline solution, but the amount present is readily obtained by distillation of the urine with sulphuric acid, estimation of the total acetone in the distillate, and subtraction of the amount of free acetone found in the undistilled urine.

In the presence of sugar the free acetone may be removed by an air current (Folin) and the acetoacetic acid then estimated by distillation. Subtraction of this result from the total acetone obtained by distillation of the unaerated urine furnishes the amount of free acetone.

The hydroxybutyric acid may also be estimated by oxidation of the residual urine in the distillation flask by Shaffer's method and subsequent estimation of the formed acetone by the new colorimetric method.

H. W. B.

Ammonia and Amino-acids in Urine. W. C. DE GRAAFF and J. E. VAN DER ZANDE (*Pharm. Weekblad*, 1916, **53**, 1378—1382).—A comparison of the method of de Jager (*Zeitsch. physiol. Chem.*, 1909, **62**, 333) for the estimation of ammonia and amino-acids in urine with that of Bonnema (*Chem. Zeit.*, 1915, **39**, 519). Both methods give consistent results, but that of Bonnema gives higher percentages of ammonia and lower percentages of amino-acids.

A. J. W.

Estimation of Urea in Blood. COMBE and MEYER-LEVI (*Ann. Chim. anal.*, 1916, **21**, 208—209; from *J. Suisse pharm.*, 1915).—A small quantity of the blood (a few drops are sufficient) is collected in a test-tube containing a dilute citrate solution, 20 c.c. of absolute alcohol are added, the mixture is shaken, and the alcoholic solution decanted from the precipitate, which is washed twice with alcohol. The alcoholic solution is treated with two drops of nitric acid, evaporated to about 2 c.c., rendered alkaline with sodium hydroxide, and mercuric nitrate solution is added as long as a precipitate forms. This precipitate is separated by filtration, the neutral filtrate is treated with a slight excess of mercuric nitrate solution, and, when the precipitate has become crystalline (this requires about thirty minutes), the mixture is submitted to

centrifugal action; the deposit is washed twice with water, then dissolved in a drop of acetic acid, and to the solution are added 10 c.c. of $N/50$-ammonium thiocyanate solution and 1 c.c. of $N/10$-zinc nitrate solution. The mixture is submitted to centrifugal action, the liquid decanted, 5 c.c. of $N/20$-silver solution are added, and the solution is titrated with $N/50$-ammonium thiocyanate solution, using ferric alum as the indicator. The weight of urea per litre of blood is $(2{\cdot}5 - A) \times 1{\cdot}272/P$, where A is number of c.c. of thiocyanate solution used and P the weight of blood taken.

W. P. S.

Estimation of Urea in Blood-serum. ED. JUSTIN MUELLER (*Chem. Zentr.*, 1916, i, 1198; from *Bull. Sci. Pharm.*, 1915, **22**, 331—334).—Details are given of an apparatus and method by means of which the proportion of urea in blood-serum may be estimated, the solution being treated with sodium hypobromite and the volume of gas liberated measured. T. H. P.

Direct Estimation of Urea and Ammonia in Muscle. JAMES B. SUMNER (*J. Biol. Chem.*, 1916, **27**, 95—101).—For the estimation of the ammonia, the coarsely chopped muscle is treated with potassium carbonate, and the ammonia transferred by aeration into a known quantity of $N/100$-acid. The urea is estimated by mixing a weighed amount of the chopped muscle with a urease solution, when the urea rapidly diffuses through the cell membranes and is wholly converted into ammonia. After thirty minutes, the mixture is treated with potassium carbonate, and the liberated ammonia removed by a strong current of air in the usual way.

Fresh muscle contains from 10 to 16 mg. of ammonia nitrogen per 100 grams of moist tissue and about an equal quantity of urea nitrogen. A slight increase in the amount of ammonia occurs when the muscle is allowed to remain for a few hours at 30°.

H. W. B.

Microchemical Distinction of Morphine from Codeine. O. TUNMANN (*Chem. Zentr.*, 1916, ii, 35; from *Apoth.-Zeit.*, 1916, **31**, 148—150).—When treated with hydriodic acid, these alkaloids yield crystals which have always the same forms and allow of the differentiation of the two bases. A little of a salt of the base is sublimed by heating on an asbestos plate, and the sublimate covered with a cover-glass, at the edge of which a drop of hydriodic acid is then introduced. A slight granular precipitate is thus formed, and this disappears on heating. When the preparation is cooled, crystals of the tetraiodide are formed immediately in the case of morphine, whereas with codeine, crystals of the tri-iodide are formed only after three to five minutes, but more rapidly in presence of a small drop of alcohol.

The morphine tetraiodide crystals are always very flat, quadrangular, mostly rectangular plates, on the average 30—50 μ broad by 80—120 μ long, and are of prismatic character and show

direct extinction and a blood-red to brownish-red colour. The bulk of the crystals are united to ladder- and step-like aggregates more than a millimetre in length, and these in their turn are combined to stars and crosses. Pleochroism is either very slight or non-existent.

Codeine tri-iodide crystals are paler, thicker, and smaller, the aggregates being not more than one-third of the size of morphine tetraiodide crystals. Single crystals ($20—50\ \mu \times 40—80\ \mu$) are very rare, and form half-moon-like triangles with a concave base and a blunted apex. The majority are twinned crystals, which always grow out on the convex side and give butterfly- and goblet-like forms, by which these crystals are recognisable at the first glance. Strong pleochroism is observed in this case. T. H. P.

Factors Connecting the Concentration and the Optical Rotatory Power of Aqueous Solutions of Nicotine. Alfred Tingle and Allan A. Ferguson (*Trans. Roy. Soc. Canada*, 1916, [iii], **10**, 19—25).—Working with a polarimeter using "j" light, the authors have carried out experiments which show: (1) that for solutions of concentration between 4 and 0·37 the rotation of aqueous nicotine solutions is in simple inverse proportion to the concentration; (2) that the presence of potassium hydroxide and potassium salts has no influence on the rotation of nicotine salts; (3) that nicotine is not lost by vaporisation when an acid solution of nicotine sulphate is evaporated. In addition, the rotation, in terms of Ventzke sugar-scale divisions, of a pure specimen of nicotine in aqueous solution was determined, and found to be -1 division ($l=200$ mm.) for every 0·2198 gram of nicotine per 100 c.c. of solution, or 1 gram of nicotine in 100 c.c. solution would read $-4·5$ divisions in a 200 mm. tube for "j" light.

T. S. Pa.

Transcopia: New Method for the Detection of Human Blood. Angelo de Dominicis (*Boll. chim. farm.*, 1916, **45**, 513—514).—Traces of blood may be transferred, without alteration of the red corpuscles, from the point of a blade, etc., to a microscope slide by means of a little dense celluloid or collodion, which is allowed to set on the blood spot and then detached by means of a lancet; to this process the name *transcopia* is given. The pellicle obtained in this way is placed on a microscope slide and covered with a cover-glass, the latter being gently pressed and the space beneath it filled with acetone saturated with eosin; other solvents and other staining agents may be employed. The best results are obtained with blood spots on metal, stone, wood, or non-absorbent surfaces in general, and thin spots or the edges of spots are the most suitable for microscopic observation. The method is also applicable where the blood stains are on textiles, paper, walls, etc.

T. H. P.

INDEX TO PATENTS.

ERRATA.

VOL. C (ABSTR., 1911).

Page Line

i. 169 12 *for* "$\begin{array}{l}C_6H_4\cdot C\cdot NHB_z \\ \| \quad\;\; \| \\ C_6H_4\cdot C\cdot OH\end{array}$" *read* "$\begin{array}{l}C_6H_4\cdot C\cdot NHB_z \\ | \quad\;\; \| \\ C_6H_4\cdot C\cdot OH.\end{array}$"

VOL. CVI (ABSTR., 1914).

Page Line Col.

891 27 ii *for* "**Emden**" *read* "**Embden.**"

VOL. CVIII (ABSTR., 1915).

Page Line

i. 820 11* *for* "nitrite" *read* "nitrile."

ii. 821 2*, ii. 824 12*, i. 835 5*, ii. 836 2, ii. 841 2* } for "*Anal. Fis. Quim. Argentina*" read "*Anal. Soc. Quim. Argentina.*"

VOL. CVIII (ABSTR., 1915).

INDEX.

Page Line Col.

ii. 854 5–7 i Delete.

ii. 878 23* i *for* "electrolytes" *read* "electrolysis."

ii. 894 20 i ,, "A., i, 744, 747" *read* "A., ii, 744, 747."

ii. 922 18 ii ,, "**Mary**, *Alexandre*. See **Albert**" *read* "**Mary**, *Albert*, and *Alexandre* **Mary**, physico-chemical studies on the synthesis of a chlorophyll pigment, A., i, 979."

ii. 1014 32 i ,, "2:6-*dimethyl*-$\Delta^{2:6}$-*octadien*-8-*al*" read "$\beta\zeta$-*dimethyl*-$\Delta^{\beta\zeta}$-*octadiene*-θ-*al*."

VOL. CX (ABSTR., 1916).

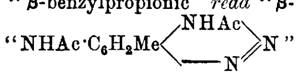
Page Line

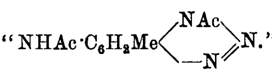
i. 27 24, 25, 26 { should read "*compounds* with 1AcOH, yellow needles, which on loss of the acetic acid yield the more deeply-coloured, orange modification of the parent substance, and with $1CCl_3\cdot CO_2H$, orange leaflets, which on loss of the trichloroacetic acid yield the yellow modification of the."

i. 68 12* for "1-*ethyl*-2-*pyrrolidyl ethyl ketone*" read "1-*ethyl*-2-*pyrrolidyl methyl ketone.*"

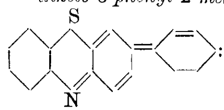
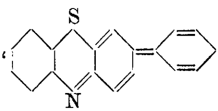
i. 75 7 *for* "acetonylacetone" *read* "acetylacetone."

i. 78 15* ,, "β-benzylpropionic" *read* "β-benzoylpropionic."

i. 82 5, 14 } ,, "" *read*

""

* From bottom.

Page	Line	
i. 102	19*	*for* "NOLLAN" *read* "NOLLAU."
i. 132	4	,, "$n\beta$ 1·45313°" *read* "$n\beta$ 1·45313."
i. 144	6, 7	,, "3:6:2′:5-tetrachlorobenzoylbenzoic" *read* "3:6:2′:5′-tetrachlorobenzoylbenzoic."
i. 145	17	,, "tetrabromobenzoyldichlorobenzoic" *read* "dichlorotetrabromobenzoylbenzoic."
i. 153	5, 6	,, "β-resorcyclic" *read* "resorcylic."
i. 160	18*–17*	*should read* "By treatment in alkaline solution with ethyl chloroformate and with phenylcarbimide."
i. 206	26	*for* "phenylbenzylmethylallyl" *read* "phenylbenzylmethylallylammonium."
i. 260	20	,, "iodomagnesium" *read* "bromomagnesium."
i. 261	2*	,, "$C_{34}H_{50}O_2Br,$," *read* "$C_{34}H_{50}O_2Br_2$."
i. 282	16	,, "$OH{\cdot}C_6H_3{<}^{OCl—CH}_{C(NH)_2\cdot CPh}$" *read* "$OH{\cdot}C_6H_3{<}^{OCl—CH}_{C(NH_2)\cdot CPh}$"
i. 284	12	,, "4:5′-*diketo*-3-*phenyl*-2-*methyl*-βγ-*indenopyran*" read "4:5-*diketo*-3-*phenyl*-2-*methyl*-βγ-*indenopyran*."
i. 289	17	,, "  " *read* "  ."
i. 290	5*	,, "$\left(\begin{matrix}CHPh\cdot CH_2 \\ NH—N\end{matrix}\!>\!C\cdot CH_2\cdot CHPh\cdot NH\cdot_2\right)$" *read* "$\left(\begin{matrix}CHPh\cdot CH_2 \\ NH—N\end{matrix}\!>\!C\cdot CH_2\cdot CHPh\cdot NH\cdot\right)_2$"
i. 316	18*	for "*diacetyldimethoxydehydrodianthranyl*" read "*diacetoxydimethoxydehydrodianthranyl.*"
i. 317	19	,, "**441**" *read* "**411.**"
i. 338	6	*insert* "D. F. T."
i. 341	2	for "*carbazinate*" read "*dithiocarbazinate.*"
i. 342	19	,, "*benzoyl*" read "*benzyl.*"
i. 343	12, 17	,, "*carbomethoxydithiocarbamate*" read "*carbomethoxydithiocarbazinate.*"
i. 345	23	,, "$\begin{matrix}N & — & N \\ \Vert & & \Vert \\ Ph\cdot C\cdot H & & NO_2\cdot C_6H_4\cdot CH_2\cdot C\cdot SMe\end{matrix}$" *read* "$\begin{matrix}N & — & N \\ \Vert & & \Vert \\ Ph\cdot C\cdot H & & NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot C\cdot SMe\end{matrix}$"
i. 368	21*	*for* "β-methyloctoic" *read* "α-methyloctoic."
i. 552	7	,, "$COMe\cdot CH_2\cdot CH_2\cdot COH$" *read* "$COMe\cdot CH_2\cdot CH_2\cdot CO_2H$."
i. 587	5	,, "IODLBAUER" *read* "JODLBAUER."
i. 623	17	,, "**Hydrogen**" *read* "**Nitrogen.**"
ii. 14	15, 17	,, "helium" *read* "neon."
ii. 303	22	,, "HUHN" *read* "KUHN."
ii. 321	bottom	*for* "C_5H_{12}" *read* "Si_5H_{12}." ,, "C_6H_{14}" *read* "Si_6H_{14}."

* From bottom.

ERRATA (*continued*).

Page	Line	
ii. 348	13	*for* "described by Lenher & Crawford (A., 1913; ii, 250)" *read* "depending on the colour of titanous salts."
ii. 433	10	,, "JOHNSTONE" *read* "JOHNSTON."
ii. 505	2, 22	,, "*physical*" read "*physikal.*"

Page	Line	Col.	
ii. 662	16*	i	*insert* "**Bary**, *Paul*, the velocity of solution of liquids in caoutchouc, A., ii, 24."
ii. 670	14	i	*delete* "**Bury**, *Paul*, etc."
ii. 744	24	i	*insert* "**Tschugaev**, *L.*, and *I.* **Tschernjaev**, the hydroxylammonia complexes of bivalent platinum, A., ii, 42."

COLLECTIVE INDEX, 1903—1912 (AUTHORS).

Page	Line	Col.	
786	11	ii	*for* "1912, A., i, 8" *read* "1912, A., i, 822."

COLLECTIVE INDEX, 1903—1912 (SUBJECTS).

Page	Line	Col.	
563	12	ii	*for* "A., i, 415" *read* "A., ii, 415."

* From bottom.